SYNTHESIS OF VARIABLE BANDGAP CONJUGATED POLYELECTROLYTES VIA METAL CATALYZED CROSS-COUPLING REACTIONS

By

MICHAEL BRIAN RAMEY

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2001

This dissertation is dedicated to James B. and Jewell Q. Ramey, and Ralph and Georgia Qualls whose lifelong work, encouragement, and love have made the construction of this dissertation possible.

ACKNOWLEDGMENTS

The greatest acknowledgment goes to my Lord and Savior, Jesus Christ, whose loving sacrifice wipes clean the imperfections of us all. My wife, Jennifer Ramey, has walked hand in hand with me throughout my growth as a Christian and scientist and without her support and love my life would not be complete. Family members mentioned in the dedication essentially gave up a large portion of their lives in order to make mine a success and that debt can never be repaid. The investment in my life was paid with the sweat of their brow and with intellectual and emotional guidance. Now that I am expecting the arrival of my first child in September 2001, I can only hope to reflect the same attitude to my son or daughter.

I would also like to thank those around me in the professional arena. Dr. John Reynolds has helped guide me through the process of becoming a Ph.D. scientist and has set an excellent example of the life of a Christian man. Dr. Kenneth Wagener has almost been like a second research advisor to me as he is available and helpful for all students who come to him in search of advice on research, professionalism, or life. The students, post-docs, and visiting scientists make the George and Josephine Polymer Research Laboratory an outstanding environment in which to work. Special thanks go out to my closest friends on the polymer floor: Jason Smith and Cameron Church who have had the pleasure of jumping through the same hoops and sharing the same experiences as members of the same entering graduate class; Dean Welsh who is a fellow NASCAR

fan, workout partner, and scientific consultant; and C.J. Dubois who is one entertaining Cajun, but respectful and competent lab co-worker.

TABLE OF CONTENTS

page

ACKNOWLEDGMENTS iii

LIST OF TABLES vii

LIST OF FIGURES viii

ABSTRACT xi

INTRODUCTION 1

The Origination of Polymer Chemistry 1
Background and Theory of Conjugated Polymers 2
Bandgap: From Dienes to Extended Conjugation Systems 3
Luminescence: Photo- and Electro- 8
Conjugated Polymers for Electroactive Applications 11
Palladium(0) Coupling Reactions 13
General Catalytic Cycles and Mechanism 14
Conjugated Polyelectrolytes 17
Scope of the Dissertation 18

CATIONIC POLY(*p*-PHENYLENE)'S 20

Introduction 20
Early Synthetic Attempts 20
Suzuki Couplings 22
Results and Discussion 25
Monomer and Model Compound Syntheses 25
Neutral Polymer Syntheses 30
Polymer Quaternization 39
Physical Properties of PPP Type Polymers 41
Conclusions 44

CATIONIC POLY(*p*-PHENYLENE-*co*-THIOPHENE)'s 47

Introduction 47
Early Synthetic Attempts 48
Optimization of the Stille Coupling Polymerization 50
Results and Discussion 54

Monomer Syntheses and Suzuki Coupling Test Reactions 54
Neutral Polymer Syntheses 59
Polymer Quaternization 65
Physical Properties of PPT Type Polymers 66
Conclusions 69

CATIONIC POLY(*p*-PHENYLENE-ETHYNYLENE)'s 71

Introduction 71
Early Synthetic Attempts 71
Palladium (0) Coupling Reactions 72
Dialkoxy-Poly(*p*-phenyleneethynylene)'s 75
Results and Discussion 78
Monomer Syntheses 78
Neutral Polymer Syntheses 87
Polymer Quaternization 94
Physical Properties of PPE Type Polymers 95
Conclusions 99

CONCLUSIONS 101

EXPERIMENTAL 107

Chapter 2 108
Chapter 3 116
Chapter 4 122

REFERENCES 132

BIOGRAPHICAL SKETCH 140

LIST OF TABLES

Table — Page

1-1. Brief Summary of Emission Wavelength for Differing Conjugated Polymer Structures..... 12

2-1. Catalyst effect on the molecular weight properties of PPP-NEt_2 polymers..... 36

2-2. Elemental Analysis results for PPP monomers and polymers..... 37

2-3. Effect of DBNEt or DINEt on the molecular weight of PPP-NEt_2 polymers..... 38

3-1. Structures of the organohalides and triflates for the Stille reactions..... 51

3-2. Structures of the organotin monomers for the Stille reactions..... 51

3-3. GC/MS results of Suzuki coupling of 2,5-thiophene diboronate ester and 4-bromotoluene..... 58

3-4. Gel permeation chromatography results for Stille coupling of PPT-NEt_2..... 61

3-5. Elemental Analysis results for PPT monomers and polymers..... 62

3-6. Summary of optical data for PPT-NEt type polymers..... 68

4-1. Elemental analysis results for PPE monomers and polymers..... 81

4-2. Summary of optical data for **PPE-OC9(20)** type polymers..... 97

LIST OF FIGURES

Figure Page

1-1. Structures of poly(*p*-phenyleneterephthalamide) (**1**), poly(benzobisthiazole) (**2**), and poly(*p*-phenylene) (**3**). 3

1-2. Application of Frost's circle to illustrate the energies of molecular orbitals within cyclic systems. 5

1-3. Band structure and density of states (DOS) diagram of a simple one dimensional metal (polyacetylene) prior to and after a Peierls distortion. 7

1-4. Geometrical relaxation of a PPV chain in response to photo- or electo- excitation. 10

1-5. Polaron, bipolaron, and singlet exciton energy levels in a non-degenerate ground-state polymer. 10

1-6. Electronic transitions in a conjugated polymer (i.e. PPV) showing both singlet and triplet states. 11

1-7. General catalytic cycle for Pd(0) cross coupling reactions. 15

2-1. Synthetic methods to poly(*p*-phenylene). 22

2-2. Suzuki coupling approaches to substituted poly(*p*-phenylene). 23

2-3. Anionic poly(*p*-phenylene)'s reported in the literature. 24

2-4. Cationic poly(*p*-phenylene)'s reported in the literature (R = hexyl). 25

2-5. Conversion of 1,4-dimethoxybenzene to 2,5-diiodohydroquinone. 26

2-6. Bromination of hydroquinone in the 2,5 positions. 27

2-7. Williamson etherification of **DIHQ** or **DBHQ**. 28

2-8. Synthesis of di-boronic phenylene reagents for use in Suzuki couplings. 29

2-9. Synthesis of neutral and cationic PPP model compounds. 30

2-10. Suzuki polymerizations for neutral alkoxy-amine containing PPP's. 31

2-11. Cl-Pd-Cl bond angle for $PdCl_2$(dppe), $PdCl_2$(dppp), and $PdCl_2$(dppf) catalysts. 34

2-12. Gel permeation chromatogram for **PPP-NEt_2(dppf)[12]** 36

2-13. Envisioned boronic reagents for a more substituted PPP-NEt_2 polymer. 38

2-14. Pd catalyzed coupling to diboronic reagents for Suzuki couplings. 38

2-15. Quaternization of PPP-NEt_2 40

2-16. UV-Vis / Emission behavior of neutral and water soluble PPP-NEt 43

2-17. Photoluminescent spectrum of **PPP-NEt_2[12]** in THF with normalized and linear emission scale 44

2-18. TGA thermograms for neutral and water soluble PPP-NEt under N_2. 45

3-1. Literature examples of phenylene-*co*-thiophene type polymers. 49

3-2. General scheme for the Stille polymerization 49

3-3. Representative polymer repeat units of Stille polymerizations. 52

3-4. Synthesis of 2,5-bis(trimethylstannyl)thiophene. 55

3-5. Synthesis of 2,5-thiophene diboronate ester. 56

3-6. Test coupling reaction of 2,5-thiophene diboronate ester and 4-bromotoluene. 57

3-7. Stille coupling polymerization scheme for PPT-NEt_2. 60

3-8. ^1H and ^{13}C NMR spectra of PPT-NEt_2[**28**] 63

3-9. Synthesis of PPT-NEt_2[**29**] via Suzuki coupling polymerization. 64

3-10. Quaternization of PPT-NEt_2 to form PPT-NEt_3+. 66

3-11. Normalized UV-Vis absorption and solution photoluminescence for PPT-NEt type polymers. 67

3-12. TGA thermograms for neutral and water soluble PPT-NEt under N_2. 69

4-1. Early synthetic methodologies toward poly(*p*-phenyleneethynylene)'s [PPE]. 72

4-2. General reaction scheme for the Heck-Cassar-Sonogashira-Hagihara reaction. 73

4-3. Activation of Pd(II) compound to active Pd(0) catalyst. 74

4-4. Synthesis of dialkoxy poly(*p*-phenyleneethynylene)'s via the Sonogashira reaction. . 75

4-5. Representative structures of synthetic modifications to poly(*p*-phenyleneethynylene)'s. 77

4-6. Williamson etherification to synthesize various 1,4-dialkoxyphenylene's. 78

4-7. Iodination of various 1,4-dialkoxybenzene's. 79

4-8. Synthesis of various 1,4-diethynylphenylene monomers. 80

4-9. Synthesis of 2,5-bis(6-bromohexyl)-1,4-diiodobenzene 83

4-10. Gas chromatography analysis of purification of 6-bromohexylmethylether (**43**) by vacuum distillation using (a) simple vigreux column and (b) spinning band column. 85

4-11. Rehahn's route to cationic PPP's. 86

4-12. Williamson etherification to "protect" bromo endgroups. 86

4-13. Envisioned application of Rehahn's strategy to PPE's. 86

4-14. General synthesis for alkoxy-amine containing PPE's. 87

4-15. ^{1}H and ^{13}C NMR of **PPE-NEt$_2$/OC9(20)[54]** in $CDCl_3$. 92

4-16. Expansion of the aromatic region of the ^{1}H NMR of **PPE-NEt$_2$/OC9(20)[54]** in $CDCl_3$. 93

4-17. Conversion of **PPE-NEt$_2$/OC9(20)[54]** to cationic polyelectrolytes. 94

4-18. Normalized UV-Vis absorption and solution photoluminescence for **PPE-OC9(20)** type polymers. 97

4-19. TGA thermograms for neutral and protonated **PPE-OC9(20)** under N_2 98

Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

SYNTHESIS OF VARIABLE BANDGAP CONJUGATED POLYELECTROLYTES VIA METAL CATALYZED CROSS-COUPLING REACTIONS

By

Michael Brian Ramey

May 2001

Chairman: Dr. John R. Reynolds
Major Department: Chemistry

Metal catalyzed coupling reactions such as the Stille, Suzuki, and Sonagashira (Heck) have become useful tools for the organic chemist over the past two decades for the formation of carbon-carbon bonds. Tolerance of functional groups, reasonable reaction temperatures, and high yields have allowed these techniques to be applied to the synthesis of conjugated polymers. These syntheses offer access to a wide variety of conjugated backbone structures that have previously been difficult to reach using traditional polymerization techniques.

Poly(*p*-phenylene) [PPP], poly(*p*-phenylene-*co*-thiophene) [PPT], and poly(*p*-phenylene-*co*-ethynylene) [PPE] electrolytes have been prepared by using one of the aforementioned coupling techniques. A methodology was applied whereby charge neutral polymers were first synthesized and then converted to the corresponding cationic polyelectrolyte. This "pre-polymer" technique allows for studies comparing neutral polymer properties (i.e., absorption, luminescence, solubility) to those of the

polyelectrolyte. Significant changes in the polymers' visible absorption and emission wavelengths occur between the differing backbone structures. The polyelectrolytes' optical transitions are shifted to higher energies (blue-shifted) versus the absorption and emission of the neutral version within the same polymer backbone type.

The effects of halogenation of the monomer, solvent type, and palladium catalyst on the molecular weight were determined for each set of neutral polymers by monitoring chain extension by gel permeation chromatography. In the case of the PPP derivatives, it was found that the Suzuki polymerization proceeds the fastest to maximum molecular weight in a DMF / aqueous media using $PdCl_2$(dppf) catalyst with di-iodinated monomer. Polymerizations using di-brominated monomers reached similar molecular weight values but only after longer reaction times. Polymer chain growth in this system was limited by the precipitation of polymer from the reaction solution and not the reactivity of the halogenated monomer. PPT polymers synthesized using the Stille reaction proceeded to highest molecular weight values in anhydrous DMF using $PdCl_2(PPh_3)_2$ catalyst and di-iodinated monomer. Triethylamine / THF solvent systems using $PdCl_2(PPh_3)_2$ catalyst with a small amount of CuI co-catalyst and di-iodinated monomer were the best conditions for the PPE Sonagashira polymerizations. Di-brominated monomers were ineffective in reaching polymeric materials when used in either Stille or Sonagashira polymerizations. The conversion procedure to the polyelectrolyte was determined to be sufficiently mild not to induce breakages of the backbone, thus allowing the molecular weight characteristics for the neutral species to be roughly applied to the polyelectrolyte.

CHAPTER 1
INTRODUCTION

The Origination of Polymer Chemistry

Over the past 100 or so years, polymer science and chemistry have evolved from early rubber and Bakelite type chemistries to extensively characterized and commercialized materials. Looking back on the early evolution of this branch of science, today's observer would find vigorous debates on the exact nature of polymers: were they linear polymers held together in long chains by covalent bonds or merely "agglomerations" of smaller molecules held together by ionic forces? Today, we know that they are indeed based on the first principle as proposed and defended by Staudinger.[1]

Necessity proved to be the mother of invention as the need to replace natural items such as silk (Nylon 6,6) and rubber (*cis*-1,4-polybutadiene), imported from foreign countries to the United States, was of utmost importance during World War II as the conflict threatened to cut off supplies. From these beginnings, the study and everyday use of man-made polymers has exploded (possibly best exemplified by the whispering of the line "Just one word: plastics" in the 1967 Hollywood movie *The Graduate*). Synthetic polymers are a major cornerstone of the entire industrial chemical world and basic research on these materials has enabled scientists to understand natural polymers, such as proteins, on deeper levels than ever before. With such broad and sweeping applications and variations throughout polymer chemistry, a complete overview of the science would be impossible; therefore, a "guided tour" will be presented herein outlining

the buildup of repeat units and properties within conjugated polymer systems (materials with alternating single and double/triple bonds). These polymers have exciting new applications for optical display markets, which could never have been envisioned during the early days of the science.

Background and Theory of Conjugated Polymers

One of the simplest organic molecules is the two carbon molecule ethene, CH_2CH_2, which exists as a gas under standard temperature and pressure. Polymerization of the molecule leads to long chains of covalently bound two carbon units, $-(CH_2CH_2)-$, termed polyethylene. As the number of covalent bonds increases, the material moves through liquid (20 repeats), waxy (100 repeats), brittle plastic (200 repeats), and tough plastic (>200-300 repeats) stages of mechanical properties. In the 100-200 repeat unit regime as chain lengths become long enough to entangle, a material with plastic qualities emerges that bridges the gap between crystallites to form tougher materials.

Most polymers have a minimum molecular weight threshold where mechanical properties do not change greatly with additional coupling. Higher molecular weights may produce polymers that are more difficult to process due to poor solubility or very high melting temperatures. A balance must be achieved for each particular polymer system to make good materials that can be molded for use. As more complicated polymer systems are envisioned, several factors control the molecular weight to solubility ratio. Side chain branching from the backbone of linear polymers reduces ordering and lowers the degree of crystallinity and has become a standard method of increasing polymer solubility. Incorporation of unsaturated bonds or aromatic rings in the backbone reduces rotational freedom of the polymer chain, thereby stiffening the chain.

Functionalized polymers capable of hydrogen bonding interactions can have lowered solubility as well.

Polymers that form extended, ribbon-like structures in solution rather than a random coil conformation are termed rigid-rod polymers. Such polymers are exemplified by poly(*p*-phenyleneterephthalamide) **1**, poly(benzobisthiazole) **2**, and poly(*p*-phenylene) **3**, shown in Figure 1-1. Polymer **1** maintains its rigid-rod nature by hydrogen bonding between chains and polymers **2** and **3** maintain the same nature by being entirely conjugated. The conjugated polymers have the unique property of being electroactive, meaning they have dielectric and spectral properties (such as luminescence) that depend on applied voltages. Because of the electroactive nature of conjugated polymers, they have become a major focus of research over the last 20 or so years. It is easy for one to focus solely on the optical properties due to the visual nature of humans; however, it is important not to forget mechanical property considerations, because solubility and processing difficulties must always be dealt with in these systems.

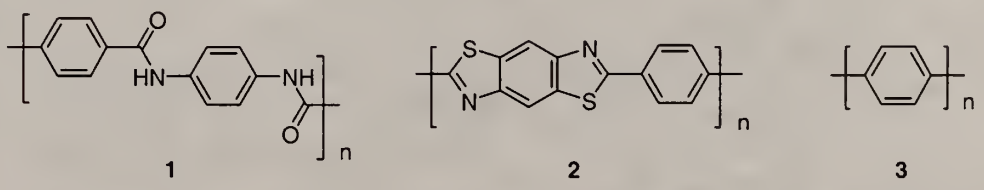


Figure 1-1. Structures of poly(*p*-phenyleneterephthalamide) (**1**), poly(benzobisthiazole) (**2**), and poly(*p*-phenylene) (**3**).

Bandgap: From Dienes to Extended Conjugation Systems

The simplest of the conjugated polymers is polyacetylene, -(CH=CH)-, which was synthesized by Ziegler-Natta polymerization of the monomeric gas.[2] The material is of

low density, fibrous, and has few defect sites.[3] Polyacetylene is intractable due to its extensive conjugation and rigid nature. Just as mechanical properties build up with additional coupling of monomer to polymer chains, electronic properties of π-conjugated polymers grow analogously. Hückel Molecular Orbital Theory provides a qualitative description of the behavior of π electrons of planar conjugated systems and can be used to explain the electronic behavior of such systems. The overlap integrals (S_{ij}) for orbitals perpendicular to one another are considered to be zero.

This method can be utilized to describe the aromaticity in benzene and can be extended to linear conjugated systems by treating them as giant cyclic structures with equally spaced carbons. Orbital energies are given by the expression

$$E = \alpha + 2\beta\cos(\frac{\pi}{N+1}J) \qquad J = 1, 2, \ldots, N \qquad (1-1)$$

where J is the orbital number, counting upward from the lowest-energy orbital $J = 1$, and N is the number of carbon atoms (also the number of basis orbitals) in the chain. The binding energy of an electron to the $2p$ orbital is related to the Coulomb integral α. The resonance integral β is related to the energy of an electron in the field of two nuclei. The maximum energy between the lowest and highest molecular orbitals is arbitrarily set at a constant value of 4β. Figure 1-2 shows the application of the Frost's circle[4] mnemonic to illustrate to energy levels for cyclobutadiene and benzene.

As the number of linearly combined atomic orbitals increase (corresponding to larger ring size in the Frost circle), it becomes clear that the energy difference between molecular orbitals becomes increasingly small. The energy to excite an electron from the HOMO to LUMO level would be insignificant relative to the thermal energy of an

electron. The orbitals would merge into a one-dimensional band, similar to the conduction bands of metals. Electrons in the highest energy occupied orbitals would be free to move into the unoccupied orbitals where they would have a high mobility. This simple model would allow for polyacetylene to be metallic with no barrier to the free movement of electrons in the system.

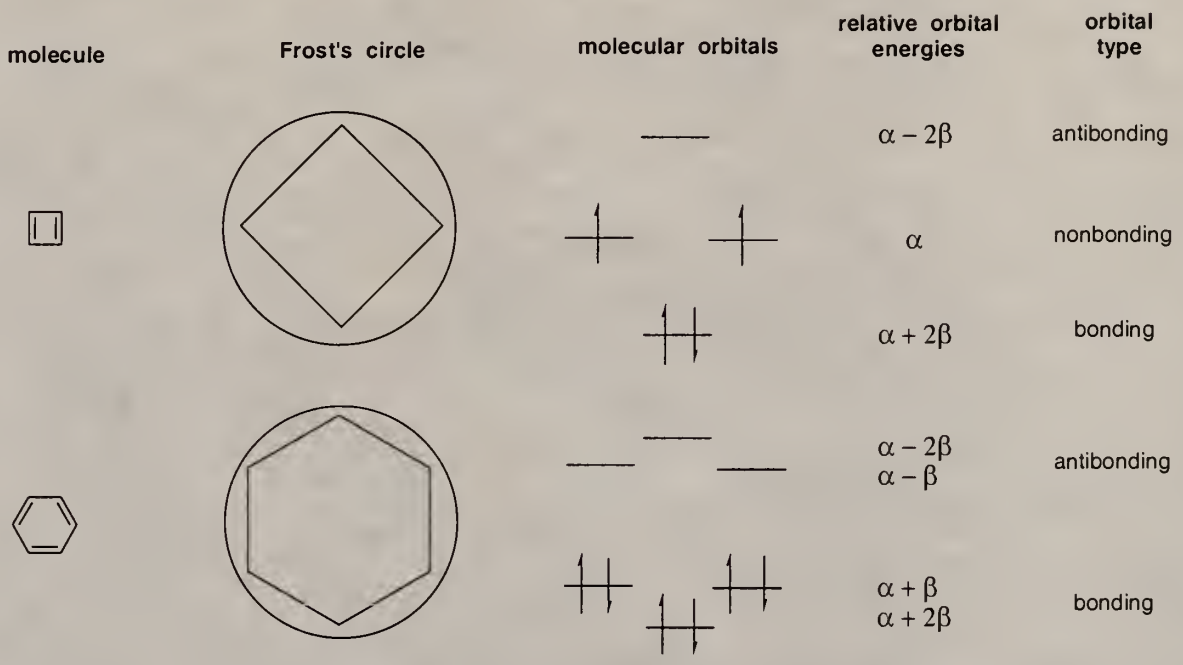


Figure 1-2. Application of Frost's circle to illustrate the energies of molecular orbitals within cyclic systems.

Experiments have proven that polyacetylene is not a metallic conductor in its neutral state. This is accounted for by analyzing the orbitals at the Fermi level. The Fermi level is the energy level which has a 50% chance of being occupied by an electron and represents the midpoint in energy of a symmetric half-filled band. The molecular orbitals at the Fermi level are close enough in energy to behave as if degenerate. The Jahn-Teller theorem[5] predicts that when degenerate orbitals are unevenly filled with

electrons, the energy of these orbitals change as a consequence of a symmetry lowering vibration. The orbitals become nondegenerate and the total energy of the system is lowered.

In solid state physics terminology, the Jahn-Teller effect is known as a Peierls distortion[6] and opens a gap in the p_z band which physically distorts the polymer chain to achieve a lower energy. Figure 1-3 graphically represents the effect of the Peierls distortion on the band structure and density of states (DOS) of polyacetylene. Figure 1-3a,b would exemplify a metallic conductor with no energy difference for electrons to migrate into the unfilled conduction band. Figure 1-3c,d demonstrates that as adjacent carbons along the polymer chain dimerize, alternate single and double bonds are formed as a discrete energy/band gap develops (E_g). The p_z band is broken into an empty conduction and a full valence band. Polyacetylene is a semiconductor ($\sigma < 10^{-5}$ S cm^{-1}) with a band-gap (Eg) of 1.4 eV.[7]

Polyacetylene can reach conductivities on the order of 10^4 S cm^{-1} by the addition of electrons into the conduction band or removal of electrons from the valence band, termed n-doping and p-doping, respectively.[8] These processes result in further structural changes in the system and defects known as solitons are formed.[9] A negative soliton corresponds to a resonance stabilized carbanion and a positive soliton corresponds to a resonance stabilized carbocation. These charged solitons move under the influence of an applied electric field.[10]

From the initial discoveries concerning the conductive and redox chemistry of polyacetylene, the field of electroactive polymers has exploded into one of the most

active research areas of polymer chemistry. The importance of the early work on polyacetylene was confirmed by the awarding of the 2000 Nobel Prize in Chemistry to

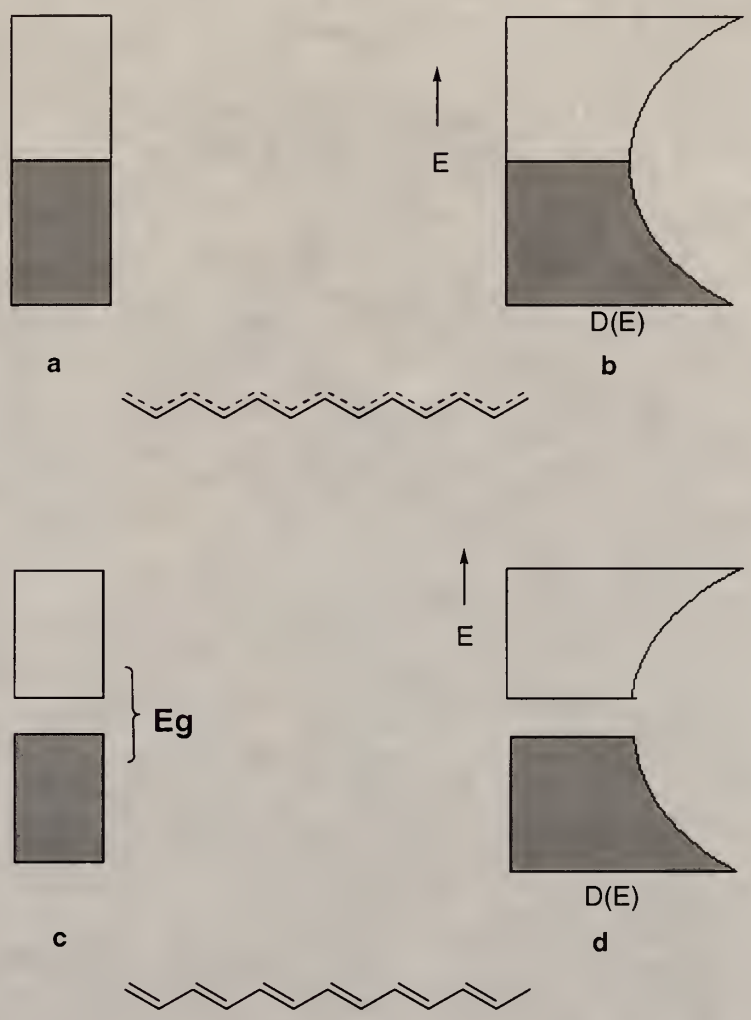


Figure 1-3. Band structure and density of states (DOS) diagram of a simple one dimensional metal (polyacetylene) prior to and after a Peierls distortion.

a) Band structure prior
b) DOS prior
c) Band structure after Peierls distortion
d) DOS after Peierls distortion.

Eg is the bandgap, which for a semiconductor such as polyacetylene is twice the activation energy for conduction.

those most responsible for the early work, Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa. The door for a myriad of creative syntheses to incorporate aromatic hydrocarbons, heterocycles, vinyl, and ethynyl groups into the backbone of π-conjugated polymers was opened by the initial work on polyacetylene. Important properties not envisioned with the discovery of polyacetylene, such as electrochromism and electroluminescence, have evolved with these newer materials. The properties and syntheses of these materials are much too varied and exciting to sufficiently cover in this dissertation, but an excellent starting reference for investigating these materials is *The Handbook of Conducting Polymers*.[11] Focus will be placed, herein, on the property of electro/photo-luminescence and the synthetic application of palladium (0) catalyzed coupling reactions to the preparation of conjugated polymers.

Luminescence: Photo- and Electro-

Much of the discussion and graphical representations presented in this introduction to the electroluminescence of conjugated polymers is based on the review of the topic by Richard H. Friend and Neil C. Greenham in "Electroluminescence in Conjugated Polymer" in *The Handbook of Conducting Polymers* (see Ref. 11). Please refer to this reference for a more complete discussion of the technical specifics for construction and properties of light emitting diodes (LED's).

Electroluminescence is the generation of light by electrical excitation and was first reported for an organic semiconductor in 1963 by the observed emission of light from single crystals of anthracene.[12] Studies on these simple electroluminescent organic semiconductors established that the process responsible for the emission of light requires the injection of electrons from one electrode and holes from the other, the capture of one

by the other (recombination), and the radiative decay of the excited state (exciton). The first example of electroluminescence from a conjugated polymer was first reported in 1990 using poly(*p*-phenylenevinylene)[PPV] as the semiconductor between metallic electrodes.[13] In LED's, a voltage bias is placed across the electrodes at a sufficient level to achieve injection of positive and negative charge carriers from opposite electrodes and upon migration, the positive and negative charges combine to form an exciton which subsequently releases energy as light.

The excitation to form an exciton may also be achieved by exposing the polymer to light of a wavelength that matches its absorption maximum and is termed photoluminescence. A singlet exciton is generated by photoexcitation across the polymer's $\pi - \pi^*$ bandgap, and radiatively decays to emit light. Emission spectra for the same polymer excited either electrically or photolytically are usually very similar, indicating that the excited state responsible for light generation is identical for both methods of excitation.

"Polaronic" excited states are formed along the polymer due to the ability of polymers to rearrange chain geometry to reduce the strain that can be produced by the charged excitations (excitons). Polyacetylene has a degenerate ground state allowing formation of soliton-like chain excitations with a nonbonding π level in the middle of the $\pi - \pi^*$ semiconductor gap.[14] In polymers with nondegenerate ground states, the two senses of bond alternation do not have equivalent energies. The charged excitations of a nondegenerate ground-state polymer are termed polarons or bipolarons and represent localized charges on the polymer chain. Figure 1-4 shows the nondegeneracy of PPV along with a schematic representation of an intrachain exciton. Two nonbonding midgap

"soliton" states form bonding and antibonding combinations, producing two gap states symmetrically displaced about the midgap (see Figure 1-5). The levels can be occupied by 0 to 4 electrons giving a positive bipolaron (bp^{2+}), positive polaron (p^{+}), polaron exciton, negative polaron (p^{-}), or negative bipolaron (bp^{2-}).

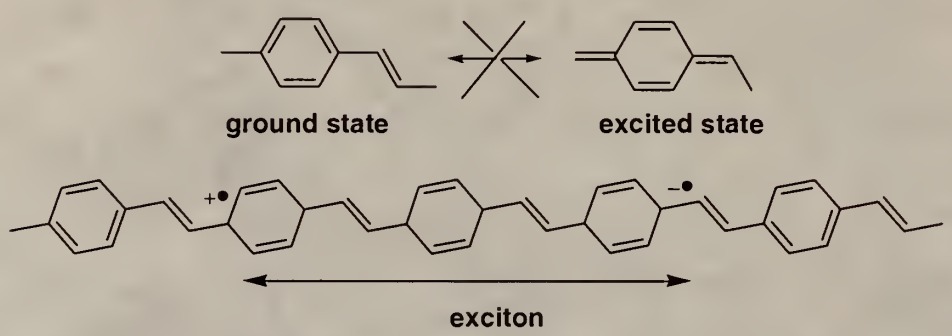


Figure 1-4. Geometrical relaxation of a PPV chain in response to photo- or electo-excitation.

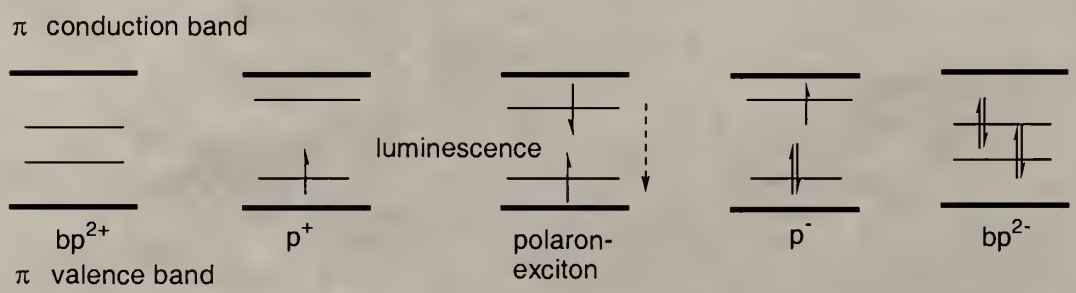


Figure 1-5. Polaron, bipolaron, and singlet exciton energy levels in a non-degenerate ground-state polymer.

Singlet and triplet excitons have been shown to exist in conjugated polymers. Taking into account both Coulonbic and electron-lattice interactions, the triplet exciton and singlet exciton are no longer of the same energy nor of the same size. The triplet exciton becomes more localized than the singlet exciton which may extend over several

polymer repeat units. Calculations have shown that the triplet exciton is stabilized by 0.65 eV with respect to the singlet exciton and is localized over not much more than a single polymer repeat unit for PPV.[15] Figure 1-6 shows the relative arrangement of ground and excited state energies for a conjugated polymer including the experimentally measured higher energy triplet (T*). Typically, excitation occurs to a singlet exciton that undergoes some vibrational release of energy and then returns to the ground state via the release of light energy. The relaxation before emission of light results in the energy of emitted light being of slightly lower energy than the energy of the π to π^* level (Stoke's shift).

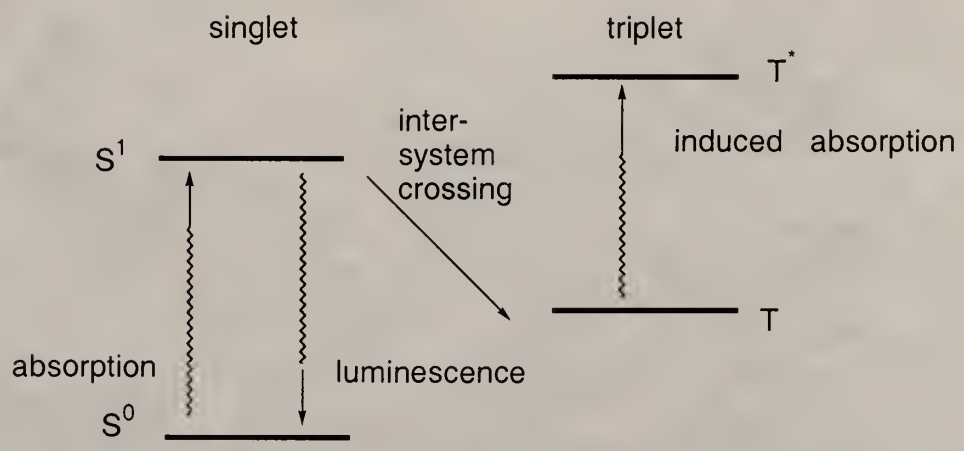
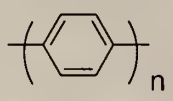
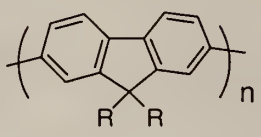
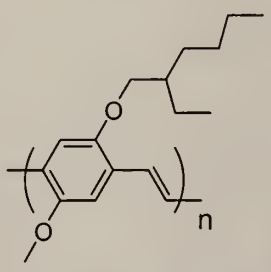
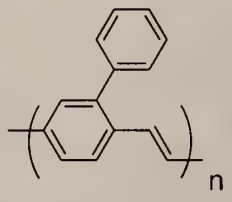
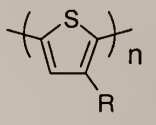


Figure 1-6. Electronic transitions in a conjugated polymer (i.e. PPV) showing both singlet and triplet states.

Conjugated Polymers for Electroactive Applications

Control of the π to π^* energy gap of a conjugated polymer is of utmost importance in order to tune the wavelength of emitted light through the visible light region. The energy gap can be modified by directly changing the type of conjugation

Table 1-1. Brief Summary of Emission Wavelength for Differing Conjugated Polymer Structures.

Structure	Name	Emission peak (nm)
	Poly(*p*-phenylene) PPP	420-465
	Polyalkylfluorene	470
	Poly(*p*-phenylenevinylene) MEH-PPV	605
	Poly(*p*-phenylenevinylene) PPPV	570
	Poly(3-alkylthiophene) P3AT	460-560

along the backbone, addition of side-chain groups with electron donating or electron withdrawing substituents, or disruption of conjugation length by insertion of non-conjugated segments. The more electron rich a system is, the farther into the lower energy, red emission portion of the visible spectrum it will be. Electron deficient polymers will emit in the higher, blue emission portion of the spectrum.

Blue emission is found in poly(*p*-phenylene) (PPP),[16] polyalkylfluorene,[17] fluorinated polyquinoline,[18] PPP-based ladder copolymers,[19] and lower gap polymers with interrupted conjugation.[20] PPV gives emission in the yellow-green light region and the emission color can be moved toward the red by substitution with electron-donating groups such as alkoxy chains at the 2- and 5- positions on the phenyl ring.[21] The very electron rich heterocycle containing polyalkylthiophenes emit in the red region of the spectrum.[22] Table 1-1 lists the polymers mentioned above with their corresponding emission peak in nanometers. It should be noted for exact LED configuration the reference for each type of polymer should be referred to as the negative electrode and transport layer material in solid state emitting devices can affect emission characteristics. The references listed represent the initial pioneering studies done on each material in the early 1990's.

Many variations and methods of device construction have been attempted over the last decade with the above polymer types and others to improve device output. Discussion of all the variations in LED construction will not be presented here due to the focus of this research being aimed at the syntheses of new conjugated polymers. In particular, a focused discussion of the palladium(0) catalyzed Suzuki, Stille, and Sonagashira coupling reactions will be conducted.

Palladium(0) Coupling Reactions

An important component was added to the toolbox of the synthetic organic chemist in the early 1970's, by the development of cross coupling reactions involving metal catalysis of organometallic species. Equation 1-3 illustrates the simple principles involved in a cross coupling reaction. R and R' are typically sp^2 hybridized carbon

$$R—M + R'—X \rightarrow R—R' \text{ [with Pd(0) catalyst]} \qquad (1\text{-}3)$$

species, M is a metal (tin, boron, etc.), and X is a halogen or triflate. Palladium catalyzed reactions of Grignard reagents was first reported by Yamamura et al.[23] and then expanded into a synthetically versatile method by Negishi et al. to include organoaluminum,[24] zinc,[25] and zirconium reagents.[26] Many other organometallic reagents have been used as nucleophiles for the cross coupling reactions including organolithiums,[27] organostannanes (Stille),[28] organosilicon,[29] and organoboron (Suzuki)[30] compounds. Terminal alkenyl (Heck)[31] and alkynyl (Sonogashira)[32] carbons are also effective for the reaction, though not organometallic species. Several good reviews are present in the literature dealing with the reactions, mechanisms, and synthetic utilities.[33]

General Catalytic Cycles and Mechanism

All of these cross coupling reactions are mechanically and synthetically similar and the general catalytic cycle will be described in this chapter. More focus on reaction specifics for the differing coupling reactions will be provided in subsequent dissertation chapters in which the chemistry involved utilizes the particular method. All of these coupling reactions proceed through a three step cycle involving 1) oxidative addition of an aryl halide (or other sp^2 C-X species) to Pd[0]; 2) transmetallation, wherein a second aryl group is transferred from the metallated species to Pd; and 3) reductive elimination of a biaryl species (see Figure 1-7). If difunctional metallated and aryl halide reagents are used, oligomeric and polymeric materials may result. Electron withdrawing groups facilitate the oxidative addition step, while the nature of the halide or leaving group affects the reaction rate following the trend I>OTf>Br>>Cl. The transmetallation step may be rate limiting if the metallated species is sterically hindered.

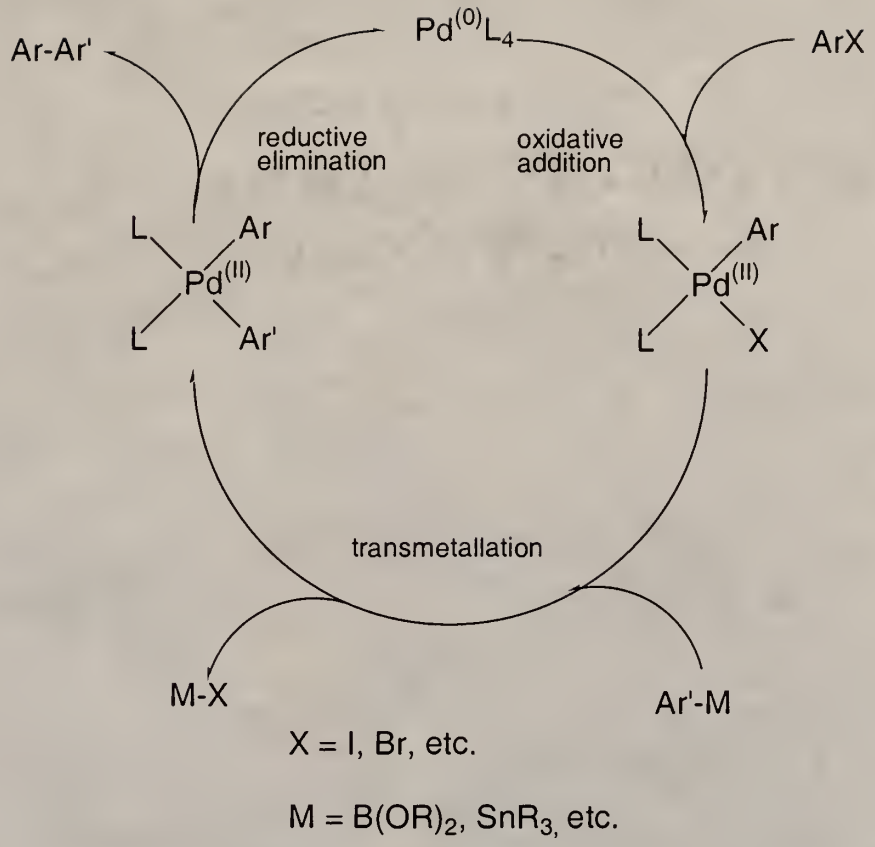


Figure 1-7. General catalytic cycle for Pd(0) cross coupling reactions.

Reactions are conducted under anaerobic conditions in a variety of solvents such as THF, DMF, and toluene. For the Suzuki reaction, water and base are added to accelerate the formation of a more active boronate anion for the transmetallation step; otherwise the other methods are performed in dry solvent. Pd(II) catalysts such as $PdCl_2(PPh_3)_2$ are usually employed in the reactions due to their general storage and handling advantages over Pd(0) catalysts, such as $Pd(PPh_3)_4$, which are air and moisture sensitive. When using a Pd(II) compound, the reduction of the Pd(II) species to Pd(0) must occur before the cycle can begin. The exact nature of this conversion is debated but may include the homo-coupling of the metallated species. Ligands present on the Pd aid

in solubility and activity of the catalyst, but can undergo ligand transfer instead of the desired aryl moiety, particularly in the case of triphenylphosphonium ligands.

Often, Stille and Suzuki polymerizations can be applied to the same desired polymers and general guidelines should be followed in making the best choice. The chemistry behind the synthesis of aryltin compounds used in Stille reactions involves the use of chlorinated alkyl tin reagents which are toxic and re-generated during the course of the reaction. Therefore, if possible the Suzuki reaction should be used. Boronic Suzuki reagents and the salts formed during the catalytic cycle are relatively "harmless." The drawback to the Suzuki reaction is that for many electron rich aryl groups, boronic esters or acids are much too unstable to withstand the numerous couplings needed for polymerization. Obviously, the Heck and Sonogashira reactions are applied specifically to the formation of vinylene and ethynylene linkages and are not alternatives to many Suzuki or Stille routes. The reagents for each are fairly stable organics and the by-products of the catalytic cycle are mineral acids.

The palladium (0) reactions hold several advantages over other polymerization techniques when used to make conjugated polymers. Many free radical polymerizations convert activated double bonds to single bonds in order to achieve the couplings, while step growth polymerizations often involve the coupling of carbon atoms to heteroatoms with an associated release of a small molecule such as H_2O. The Pd catalysts are generally stable and tolerate most functional groups, allowing a wide range of polymerization possibilities. Many complex repeat unit structures can be constructed by mixing different ratios of metal and halogenated reagents. Of course, overall a stoichiometric balance (1:1) of total halogen to metal functionality must be maintained as

these are step growth polymerizations. Catalyst residues and by-products are easily removed from the polymer product.

In the synthesis of conjugated polymers, several factors influence ultimate molecular weight properties. A balance must be maintained in a polymerization between a solvent that will keep the polymer chain in solution, so that additional couplings can be performed, and that will also solubilize the Pd catalyst so that it remains active. Chain growth is terminated by premature polymer precipitation. In general, DMF, THF, and toluene are effective solvents for the coupling reactions, with DMF able to stabilize the catalysts the most due to its coordination ability. The polarity of the solvent should match the polarity of the polymer to best keep it in solution. Temperatures must be carefully monitored as excess thermal energy can degrade the catalyst and promote the degradation of the active functionalities at the end of the polymer chains, thereby terminating chain extension. Temperatures at or below 80 ^{0}C are commonly used.

Conjugated Polyelectrolytes

As mentioned earlier, one important issue in the conjugated polymer field is that of processability. Traditionally, branched or long alkyl side chains are added to conjugated polymers to increase solubility. Although this is effective, chlorinated and high boiling solvents are often necessary to dissolve the polymers. One approach to overcoming this difficulty is to create polar conjugated polymers that are water soluble. The interesting luminescent properties mentioned previously will still be present, but now the polymers may be processed from the more environmentally and industrially friendly solvents, such as ethanol, water, etc. Side chains can be functionalized with carboxylate, sulfonate, and quaternized ammonium groups to achieve the water solubility.

There are also numerous chain extension and folding effects to be studied that are unique to polyelectrolytes. Flexible polyelectrolytes have been the focus of a considerable amount of research for many decades.[34] Decreasing the ionic strength of a dilute aqueous solution of polyelectrolyte leads to an expansion of the polymer coils and an increase of solution viscosity due to strong intra- and inter-molecular forces. Separation of the intra- versus inter- molecular forces is a difficult experimental task and only recently has the understanding of the single chain behavior of flexible polyelectrolytes been achieved by Monte Carlo simulations.[35]

Conjugated, stiff-chain polyelectrolyes remain in an extended conformation regardless of the ionic strength of the solution. Effects observed from lowering the ionic strength of the system must therefore be due to intermolecular forces. Conjugated polyelectrolytes represent interesting models for studying the screened coulombic interactions in polymeric systems. Interesting applications may also be available for these materials in membrane manufacturing.[36] Specifics and references for literature examples of conjugated polyelectrolytes synthesized by palladium (0) catalysis will be given in the introduction to Chapter 2.

Scope of the Dissertation

This body of work focuses on incorporation of quaternized 2,5-dialkoxyamine-phenylene or quaternized 2,5-dialkylamine-phenylene salt moieties into the backbone of conjugated polymers. Suzuki, Stille, Sonagashira (Heck), and ADIMET polymerization techniques will be used to synthesize neutral polymers of the following types: poly(*p*-phenylene)[**PPP**], poly(*p*-phenylene-*co*-thiophene)[**PPT**], and poly(*p*-phenylene-*co*-ethynylene)[**PPE**], whereby the phenylene portion of the repeat unit is initially

synthesized with neutral alkoxy-triethylamine or alkylbromide side chains. These neutral polymers can be analyzed using traditional techniques (GPC, NMR, etc.) and will possess absorption and luminescence wavelengths that vary over the visible wavelength range based on the electronic makeup of the backbone.

Alkoxy-triethylamine containing polymers were treated with bromoethane to form the cationic dibromide salt of the original polymer. Likewise, the alkylbromide containing polymers were treated with triethylamine to achieve the desired polyelectrolytes. Molecular weight characteristics of the neutral polymer can be approximately applied to the polyelectrolytes, since the treatments of the neutral polymer do not break backbone linkages. Optical properties will be extensively investigated focusing on the emission, absorption, and electrochromic responses from both the neutral and water soluble polymers in solution and as prepared films

CHAPTER 2
CATIONIC POLY(*p*-PHENYLENE)'S

Introduction

Early Synthetic Attempts

Poly(*p*-phenylene) (PPP) has long been a synthetic target for polymer chemists due to theoretical calculations and observations on ill-defined materials[37] that show PPP to possess good mechanical strength and high chemical resistivity.[38] Possibly, the most important property of PPP is its ability to be used as a blue emitter in electroluminescent devices.[39] The advantages of using a polymer to emit light in the consumer electronics industry are immense, as the more numerous polymer processing techniques allow for the creation of "flat panel" computer and high definition television screens unavailable with traditional materials and techniques. A thin film of PPP is placed between a high work function anode (indium tin oxide coated glass) and a low work function cathode (calcium). Under appropriate forward bias, holes and electrons are injected into the polymer film, resulting in the formation of positive polarons on one side of the film and negative polarons on the opposite side. The polarons migrate toward each other and a singlet exiton is formed resulting in the emission of blue light.

Two major factors have hindered the synthesis of PPP. As the number of rings in an unsubstituted, linear "pure PPP" type polymer increase, solubility of the resulting chain diminishes quickly, leading to an insoluble, intractable polymer that is of little or no use. However, the methodology applied to solubilizing PPP can result in materials

that do not reflect the characteristics of "pure PPP". Thermal, mechanical, and chemical stability are reduced and the optical absorption and emission wavelengths are shifted from the expected values. Nevertheless, the molecular weight enhancements and solubility of resulting substituted PPP's often outweigh the property differences between themselves and "pure PPP".

A second hindrance to PPP synthesis is that traditional polymerization techniques are not designed to grow a chain via carbon-carbon bond formation, but typically via carbon-heteroatom (oxygen or nitrogen) coupling. Often the somewhat "exotic" methods used to create PPP actually enhance side reactions leading to structurally poor polymers. Electrochemical polymerizations have been attempted both oxidatively with 1,4-dialkoxybenzenes[40] and reductively with 1,4-dihalobenzenes in the presence of a nickel catalyst.[41] Chemical oxidation polymerizations have been conducted with cupric chloride (Figure 2-1a).[42] Thermal conversion of radically[43] or transition metal polymerized[44] protected 5,6-dihydroxy-1,3-cyclohexadiene to unsubstituted PPP overcame solubility difficulties with soluble "pre-polymer" intermediates that can be processed and subsequently converted to "pure PPP" (Figure 2–1b). Thermal cyclization of enediynes and *o*-phenyldiynes gave PPP's and poly(1,4-naphthylenes), respectively (Figure 2-1c).[45] Nickel catalyzed Grignard couplings of 1,4-dibromobenzene have also been performed by Yamamoto et al. (Figure 2-1d).[46] The Grignard coupling route provided structurally pure PPP oligomers. This mild route was promising, but termination by inherent chemistry or precipitation of the growing polymer negated higher molecular weights. Attachment of alkyl side chains led to a more homogeneous polymerization and higher degrees of polymerization. Nickel catalyzed homocoupling of dichloro-,[47]

di(methanesulfonyl)-,[48] and di(trifluoromethanesulfonyl) benzenes[49] in the presence of excess zinc have afforded functionalized PPP's (Figure 2-1e,f).

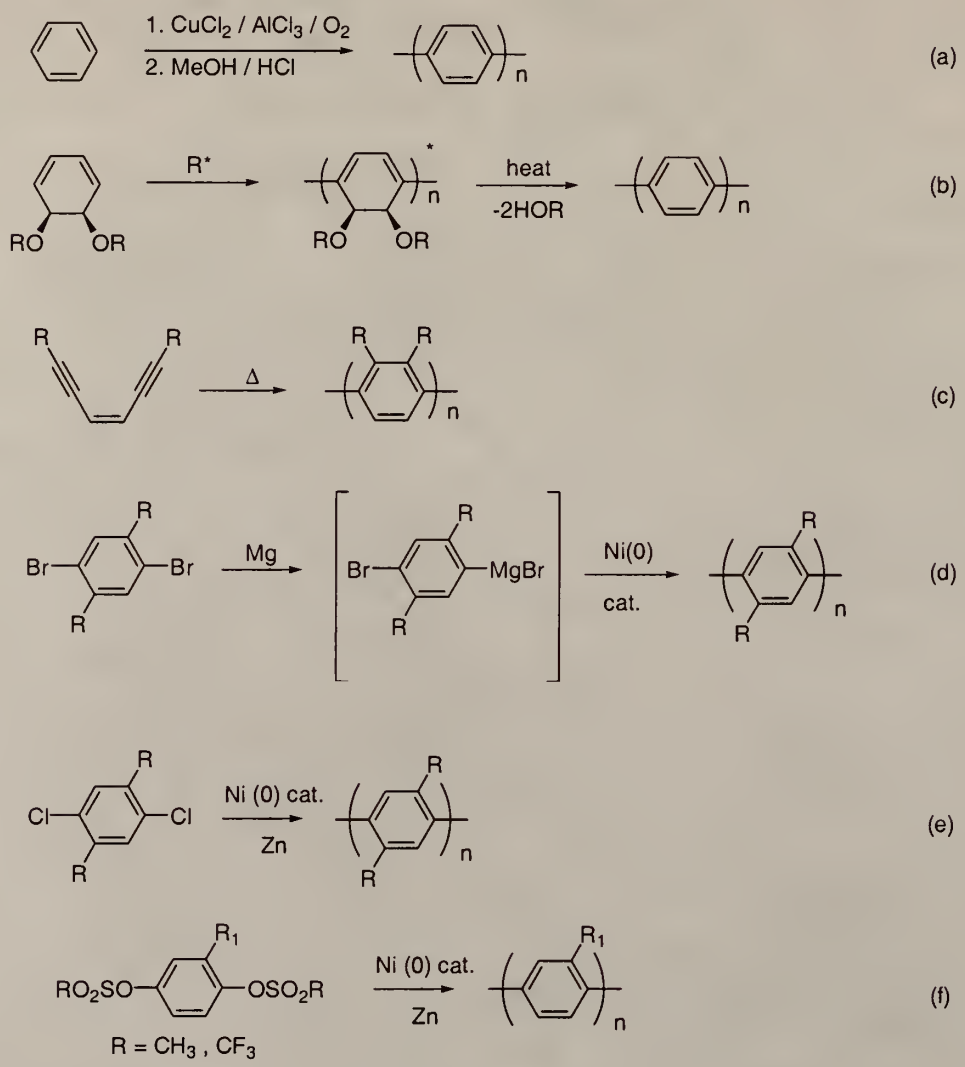


Figure 2-1. Synthetic methods to poly(*p*-phenylene).

Suzuki Couplings

A major improvement in PPP synthesis came in 1989 when Rehahn and coworkers applied the more reactive Suzuki coupling reaction methodology to the

polymerization.[50,51] A-B polymerization of 4-bromo-2,5-dialkylbenzeneboronic acids and AA/BB polymerization of 1,4-dibromo-2,5-dialkylbenzeneboronic acids was performed (Figure 2-2). Chain lengths of 100 rings were achieved leading to processable, substituted PPP's.[52]

The success of the Suzuki reaction with its use of less electropositive boron reagents, high yield couplings, and tolerance for mixed aqueous / organic solvent systems opened the door to a variety of functionalized PPP's hitherto unreachable. One of the most interesting sub-fields to arise from this methodology was the synthesis of conjugated, rigid polyelectrolytes. The first rod-like polyelectrolytes were reported in the early 1980's and were based upon poly(1,4-phenylenebenzobisoxazole) and poly(1,4-phenylenebenzobisthiazole).[53] Careful incorporation of anionic or cationic functionality into a PPP yields a material that possesses the beneficial properties of a conjugated polymer with the aqueous solubility and processability of a polyelectrolyte. The environmental utility of aqueous processing techniques applicable to polyelectrolytes is a potential advantage of these materials for use in an industrial setting. Carboxylate (Figure 2-3a,b),[54] sulfonate (Figure 2-3c),[55] and sulfonatopropoxy groups (Figure 2-3d)[56] have been used to create anionic PPP polyelectrolytes.

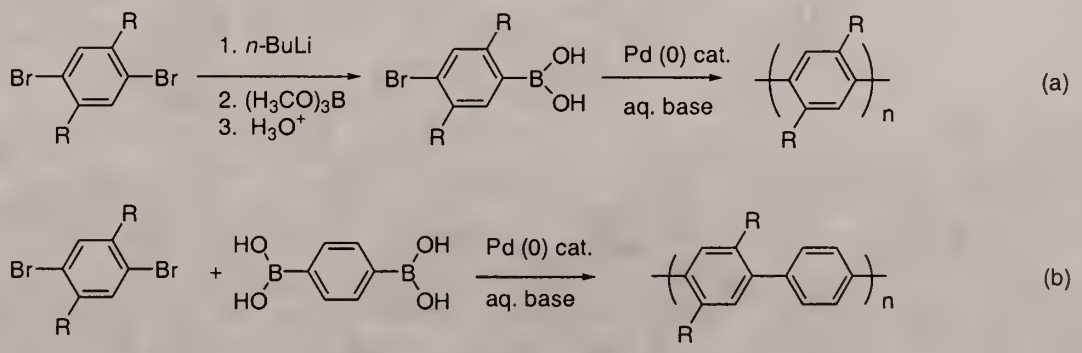


Figure 2-2. Suzuki coupling approaches to substituted poly(*p*-phenylene).

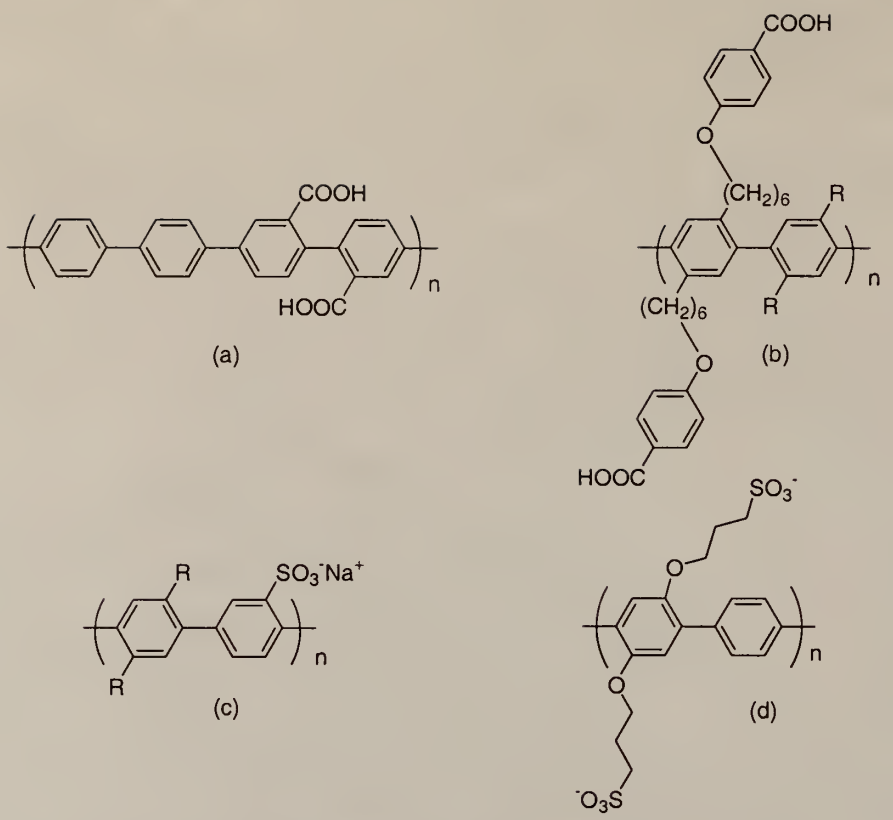


Figure 2-3. Anionic poly(*p*-phenylene)'s reported in the literature.

Highly charged cationic ammonium and pyridinium PPP polyelectrolytes were reported in the mid 1990's by Rehahn and co-workers (Figure 2-4a,b).[57] Dr. Peter B. Balanda of the Reynolds' research group used an alternate methodology to include cationic quaternary ammonium salt side chains into a PPP backbone (Figure 2-4c).[58] Poly[2,5-bis(2-{*N,N,N*-triethylammonium}-1-oxapropyl)-1,4-phenylene-*alt*-1,4-phenylene] dibromide (PPP-NEt_3+) was synthesized via a Suzuki protocol. The polymer was used in the assembly of blue emitting solid state devices via layer-by-layer polyelectrolyte self-assembly with sulfonatopropoxy PPP.[59] The material also proved very useful as a buffer layer for hybrid ink jet printed LED's using sulfonatopropoxy substituted poly(phenylene-vinylenes).[60]

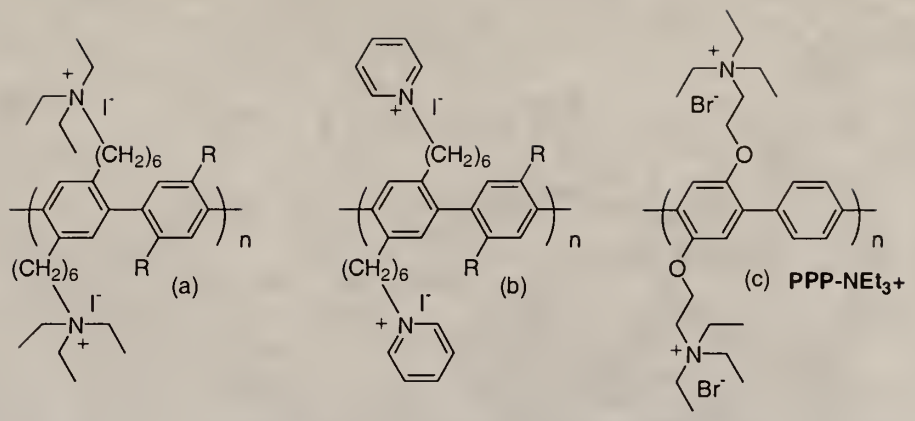


Figure 2-4. Cationic poly(*p*-phenylene)'s reported in the literature (R = hexyl).

Due to the important applications available for PPP-NEt_3+, it was evident that a closer inspection of the synthesis, along with scale-up procedures was needed. In particular, a focused look at a new palladium catalyst with stabilizing ligands and higher reactivity was a primary concern. Other synthetic investigations to be accomplished were the effect of the halogenated monomer on the molecular weight of the polymer and the effect of more unsubstituted phenylene rings in the polymer backbone. With more unsubstituted phenylene rings, a system that resembles "pure PPP" better might be created, but problems of solubility could arise also. The results and discussion following will address these aspects in greater detail.

Results and Discussion

Monomer and Model Compound Syntheses

Previous work had shown that the most promising route for the cationic water soluble PPP synthesis was to first create a neutral PPP analog and then quaternize the amine sites post polymerization. Figures 2-5 and 2-6 show the syntheses of 2,5-diiodohydroquinone and 2,5-dibromohydroquinone, respectively. 1,4-dimethoxybenzene

(**4**) was iodonated under acidic conditions using potassium periodate, iodine, and a mixed solvent system consisting of 90:7:3 HOAc/ H_2O/ H_2SO_4 by volume with heating to yield 2,5-dimethoxy-1,4-diiodobenzene (**5**).[61] Compound **5** was reacted with boron tribromide in methylene chloride at –78 ^{0}C, producing 2,5-diiodohydroquinone (**DIHQ**).[62] It should be noted that boron tribromide is a very reactive reagent with large amounts of HBr gas liberated during the aqueous workup of the reaction. **DIHQ** is recovered as a crude brown solid. Recrystallization from THF and hexane affords colorless crystals of pure product. Both steps are high yielding (81% and 76%) with an overall 62% yield based on starting material **4**. Analysis of the crude material by ^{1}H NMR shows the only organic product was the desired compound **4**. It was later found that use of this brown material was sufficient for the Williamson etherifications to follow. 90 % yield of the crude material was obtained.

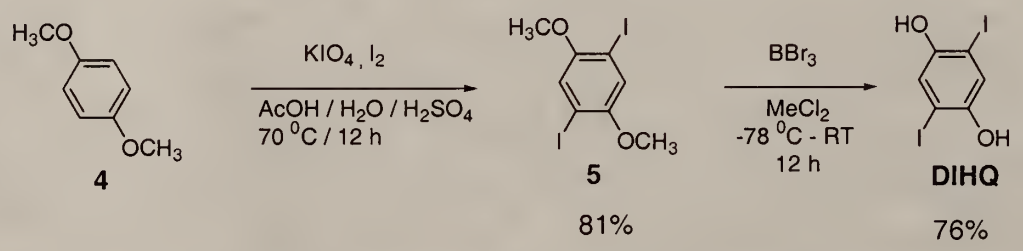


Figure 2-5. Conversion of 1,4-dimethoxybenzene to 2,5-diiodohydroquinone.

2,5-dibromohydroquinone (**DBHQ**) was synthesized in 40% yield from the direct bromination of hydroquinone (**6**) in methylene chloride and acetic acid. The reaction proceeds through three stages. The initial setup involves the suspension of hydroquinone in the solvent system. As the first equivalent of bromine is added, the resulting monobrominated species enters solution and as the second bromine adds to the phenyl ring, the desired product precipitates out of solution making product recovery a simple

matter of filtration. The reaction's lower yield is probably a result of some **DBHQ** remaining dissolved in the solvent. No attempts were made to recover this "lost" material. Recrystallization of the slightly pink crude product from a hot 4:1 (v/v) water to isopropanol solvent solution removed the undesired impurities.

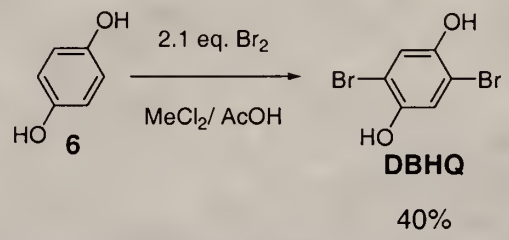
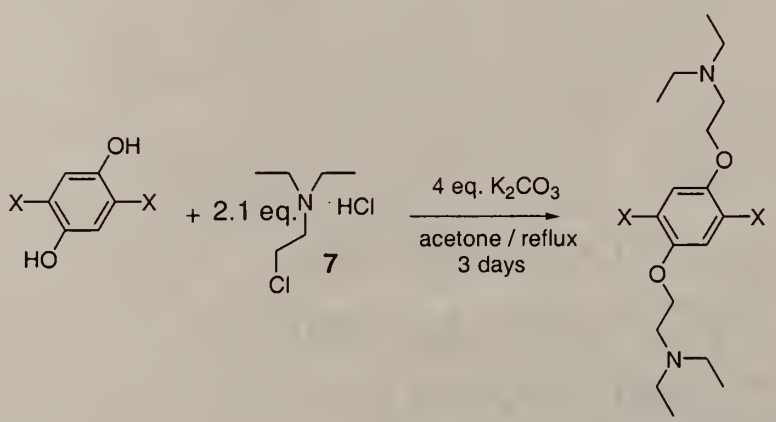


Figure 2-6. Bromination of hydroquinone in the 2,5 positions.

DIHQ and **DBHQ** were subjected to Williamson etherification conditions in refluxing acetone with 2.1 equivalents of 2-chlorotriethylamine hydrochloride (**7**) and 4.0 equivalents of K_2CO_3 for three days, as outlined in Figure 2-7, to produce the desired 1,4-dihalo-2,5-dialkoxyamine phenylene monomers, **DINEt** and **DBNEt.** Four equivalents of K_2CO_3 were necessary for deprotonation of the hydroquinone and the hydrochloride salt of the 2-chlorotriethylamine reagent which was deprotonated in situ. Isolation of the organic chlorinated amine would be difficult as cyclization to the aziridinium ion would likely occur. Grinding of the K_2CO_3 by mortar and pestle, followed by drying in an oven overnight, generally increased yields by 10%. The monomers were isolated and recrystallized twice from methanol / water to achieve maximum purity and dried over $CaSO_4$ under vacuum to ensure dryness for the accurate mass measurements necessary for step growth polymerizations. **DBNEt** was recovered in lower yield due to larger amounts of material being lost during the recrystallization steps.

Figure 2-8 outlines the preparation of various boronic reagents to be used in conjunction with **DBNEt** and **DINEt** in the Suzuki polymerizations to follow. The general reaction for all boronic species proceeds via the formation of the di-Grignard reagent of dibromo-benzene or dibromo-biphenyl,[63,64] followed by quenching with trimethyl borate. The boronate intermediate can be treated with aqueous acid to form the diboronic acid or with neopentyl glycol in a transesterification manner to produce the diboronic ester. Drying of the hydroscopic boronic acid is troublesome, and with the exact mass balance requirements necessary for polymerizations, the easily stored and purified boronic ester was preferred. The reactions are carried out in one pot with overall yields ranging from 30-40 %. Isolating the boronic acid, followed by transesterification using benzene to azeotropically distill off the H_2O by-product did not improve yields substantially (5% gain).



X	Product	%Yield
I	**DINEt**	75
Br	**DBNEt**	38

Figure 2-7. Williamson etherification of **DIHQ** or **DBHQ**.

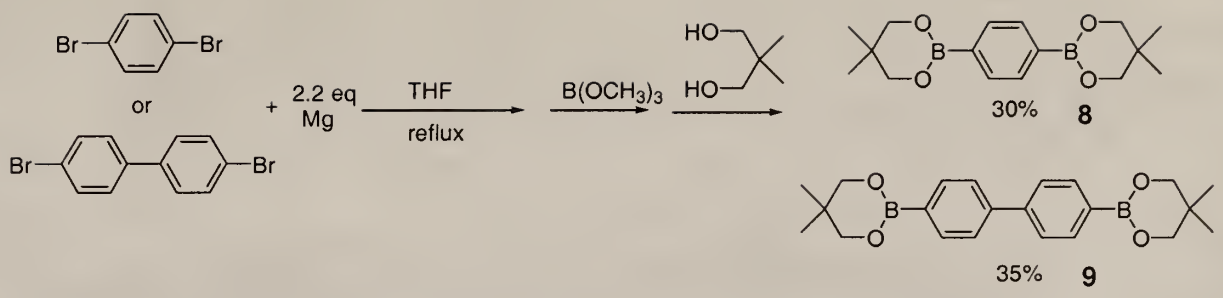


Figure 2-8. Synthesis of di-boronic phenylene reagents for use in Suzuki couplings.

Figure 2-9 outlines the preparation of a three ring model compound that was used as a guide for assigning peaks in the ^{1}H and ^{13}C NMR of subsequent polymers and also as a standard for luminescence sensing studies conducted with Dr. Kirk Schanze and Benjamin Harrison at the University of Florida.[65] Phenylboronic acid and $Pd(OAc)_2$ were used as purchased from Aldrich Chemical Company. Contamination of the product with Pd(0) does occur when using $Pd(OAc)_2$, as it lacks solubilizing ligands to keep the catalyst from precipitating. This will be a more difficult issue to address in the polymer syntheses to follow, but the contamination could easily be removed from the low molecular weight compound, **10**, by the addition of decolorizing carbon and filtration through sebaceous earth (Celite). Quaternization of compound **10** was achieved by stirring in THF and bromoethane at 40 ^{0}C for 3 days. During the course of the reaction, the desired product, **11**, precipitated out of solution. NMR peak values for both can be found in Chapter 5 (Experimental) of the dissertation. As expected, compounds **10** and **11** display extreme solubility differences. Compound **10** is soluble in relatively non-polar solvents such as halogenated organics ($CHCl_3$ and CH_2Cl_2) and the more polar THF, while compound **11** is soluble in very polar solvents such as acetonitrile and water.

Both ^{1}H NMR integration and elemental analysis (22.54 % Br) indicate a nearly quantitative level of quaternization.

Neutral Polymer Syntheses

The general Suzuki polymerization is outlined in Figure 2-10. The dialkoxyamine-dihalogenated benzene monomer, boronic reagent, Pd catalyst of choice, and mild base such as K_2CO_3, Na_2CO_3, or $NaHCO_3$ are stirred in a mixed aqueous / organic (THF, DMF, acetone) solvent system with heating to 70 ^{0}C. Special care is taken to ensure that the reaction vessel and solvents are fully degassed with Ar prior to addition of the catalyst and the reaction conducted under a blanket of the inert gas. Atmospheric O_2 in the reaction may contribute to oxidation of the Pd catalyst and decrease its catalytic activity and/or increase the rate of homocoupling of the boronic reagents.[66]

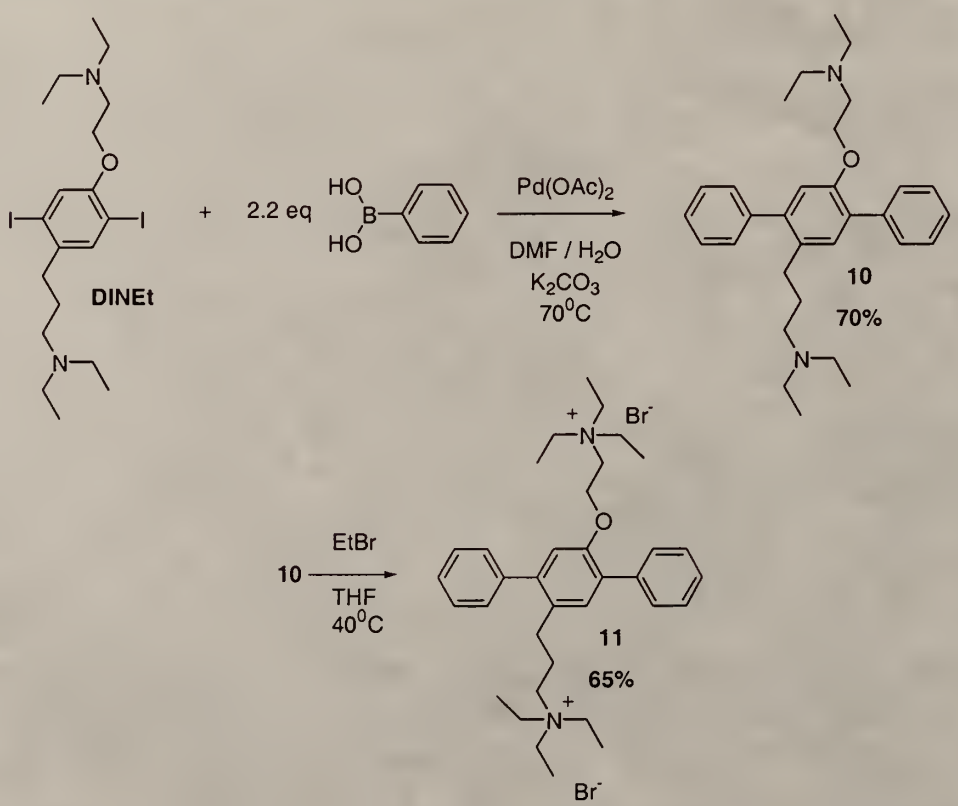


Figure 2-9. Synthesis of neutral and cationic PPP model compounds.

The original polymerizations were conducted by Dr. Peter Balanda and focused on the synthesis of **PPP-NEt$_2$** These initial synthetic investigations used **DBNEt**, $Pd(OAc)_2$ as the catalyst, with DMF, THF, and acetone as solvents. Usable polymeric materials were synthesized, with DMF polymerizations giving the highest molecular weights by GPC. Several obstacles remained. Using $Pd(OAc)_2$ as catalyst resulted in the precipitation of black, metallic Pd into solution and contamination of the polymer. Removal of this impurity often proved difficult, if not impossible, and some loss of the polymer was inevitable.

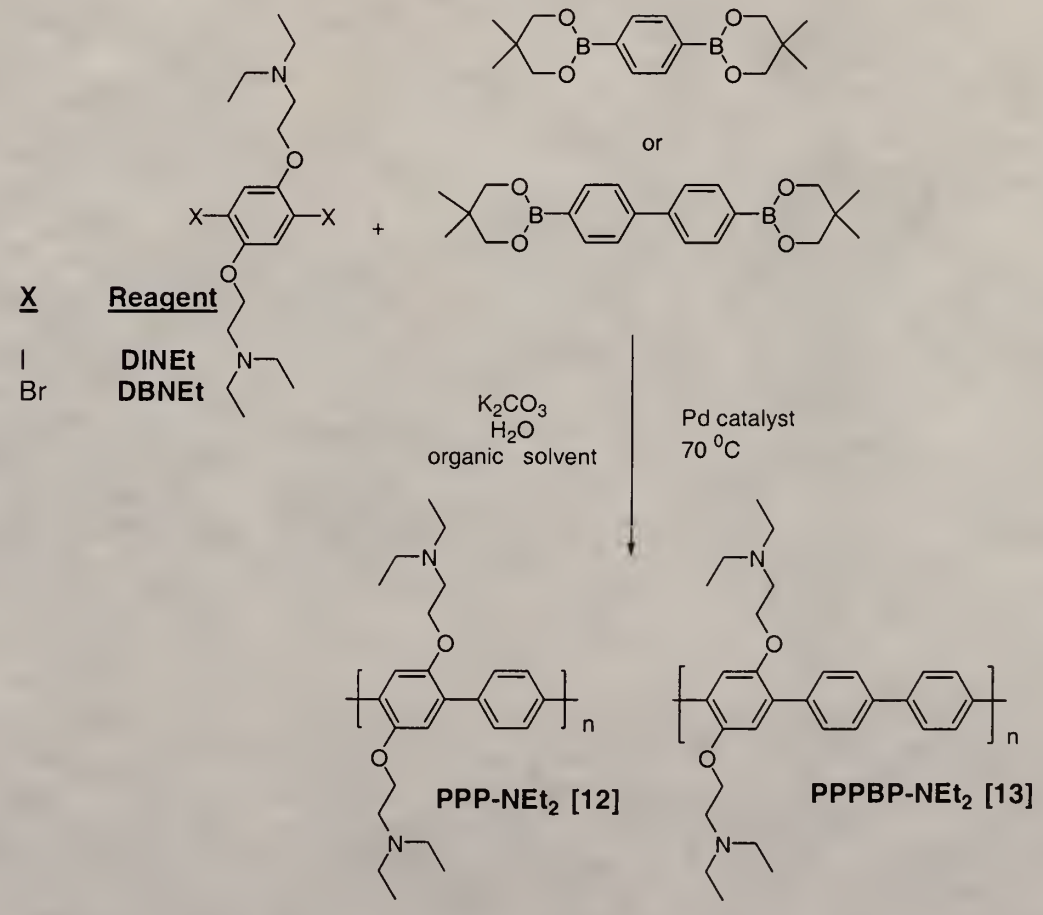


Figure 2-10. Suzuki polymerizations for neutral alkoxy-amine containing PPP's.

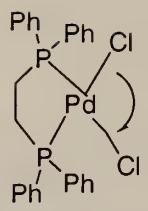
Kowitz and Wegner published results from Suzuki polymerizations using the more active dichloro[1,1'-bis(diphenylphosphino)ferrocene] palladium (II) [$PdCl_2$(dppf)] as catalyst in a THF based solution at room temperature with very high molecular weights and percent conversion to polymer.[67] The methodologies presented in reference 30 were applied to the synthesis of the amine substituted **PPP-NEt_2**.

The synthesis of $PdCl_2$(dppf) was first reported in 1984 by Hayashi et al.[68] The $PdCl_2$(dppf) has two advantages over $Pd(OAc)_2$. The dppf [diphenylphosphino ferrocene] ligand provides solubility to the catalyst as the polymerization proceeds, thus preventing contamination of the polymer with black Pd(0). With one objective to increase scale of the reaction, contamination must be avoided to prevent loss of product during "cleaning" steps. A second advantage is that palladium catalysts with bidentate phosphine ligands are more efficient catalysts than those with unidentate phosphines. The bidentate phosphine ligands create a unique geometry of the catalyst, minimizing the angle between the chlorine ligands and somewhat lengthening the palladium to phosphine bond distance. The bond lengthening reduces steric crowding between the phosphines and the palladium center. The Cl-Pd-Cl bond angle for two common palladium catalysts with bidentate ligands, dichloro[1,2-bis(diphenylphosphino)-ethane] palladium (II) [$PdCl_2$(dppe)] and dichloro[1,3-bis(diphenylphosphino)-propane] palladium (II) [$PdCl_2$(dppp)][69], along with $PdCl_2$(dppf) are shown in Figure 2–11. $PdCl_2$(dppf) has the smallest Cl-Pd-Cl bond angle of the three catalysts (87.8^0). Experiments by Hiyashi and coworkers revealed a direct relationship between the Cl-Pd-Cl bond angle and catalyst efficiency.[32] The two chlorine ligands occupy the sites where the species to be coupled will eventually reside before reductive elimination. The reduced angle leads to a rate

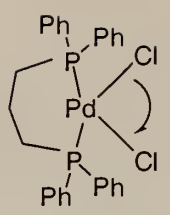
increase in the reductive elimination step, which is often the rate limiting step in Suzuki couplings, thus increasing the overall rate of the reaction.

Polymerizations of bisneopentylglycol-1,4-phenylenediboronate and **DBNEt** with $PdCl_2$(dppf) in THF / aq. $NaHCO_3$ at 75 ^{0}C for 3 days yielded improvements over previous work [**PPP-NEt_2(dppf)[12]**] . A polymer with higher molecular weight, Mn=18,700 g/mol [compared to 15,900 g/mol for $Pd(OAc)_2$ in DMF polymer **PPP-NEt_2(Br-72)[14]**], and lower polydispersity index of 1.18 was synthesized (see Table 2-1). Elemental analysis for the polymers and other compounds discussed throughout this chapter are shown in Table 2-2. Figure 2-12 shows the GPC trace for **PPP-NEt_2(dppf)[12]**. GPC traces for the other **PPP-NEt_2** polymers are similar with retention time and peak width varying for molecular weight and polydispersity, respectively. Scale up by a factor of 2 to 3 times the original scale was successful using the $PdCl_2$(dppf) catalyst as well as prevention of Pd(0) contamination. Data shown in Table 2-1 for the $Pd(OAc)_2$ polymers was taken from the dissertation of Dr. Peter Balanda. Subsequent polymerizations conducted using $Pd(OAc)_2$ reproduced this data within experimental errors. It should be noted that the low polydispersity found for the $PdCl_2$(dppf) is an effect of the polymer isolation procedures, which in all likelihood fractionated off some lower molecular weight species. Suzuki polymerizations should behave like traditional condensation polymerizations with statistically governed polydispersities of 2.

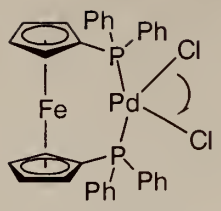
It was further believed that the use of the more active iodinated species, **DINEt**, would lead to an increase in molecular weight. Using identical protocols, reactions were conducted to couple **DINEt** or **DBNEt** with bisneopentylglycol-1,4-phenylene diboronate (**8**) via Suzuki protocol. Both reactions were quenched by precipitation into



$PdCl_2$(dppe)



$PdCl_2$(dppp)



$PdCl_2$(dppf)

Cl-Pd-Cl Bond Angle	94.2^0	90.8^0	87.8^0

Figure 2-11. Cl-Pd-Cl bond angle for $PdCl_2$(dppe), $PdCl_2$(dppp), and $PdCl_2$(dppf) catalysts.

MeOH after 3 hours. GPC results in chloroform (vs. PS standards) revealed low molecular weight oligomers ($\overline{M}_n$ < 1,500 g mol^{-1} , multi-modal) for the reaction usingthe dibromonated species [**PPP-NEt_2(Br-3)**]. The reaction using the diiodonated reagent [**PPP-NEt_2(I-3)[15]**] reached a $\overline{M}_n$ = 10,900 g mol^{-1} with a continuous polymeric distribution. Published results[22b] using **DBNEt** in the reaction for 72 hours showed a $\overline{M}_n$ = 15,900 g mol^{-1} for the resulting polymer [**PPP-NEt_2(Br-72)[14]**]. The elemental analysis and GPC results are summarized in Tables 2-2 and 2-3, respectively. Longer reaction times (complete polymerization stopped after 24 hours) with **DINEt** [**PPP-NEt_2 (I-24)[16]** ; $\overline{M}_n$ = 15,300 g mol^{-1}] approached the molecular weight values reported for **PPP- NEt_2(Br-72)[14]**. The use of **DINEt** leads to the formation of a polymer with similar molecular weight properties to **PPP-NEt_2(Br-72)[14]** in a shorter amount of time. Once the polymer has reached a certain molecular weight, it begins to precipitate out of solution, stopping polymer growth, and negating the advantages of the more reactive iodine reagent at longer reaction times.

In order to gain insight into a polymer that mimics "true" PPP more accurately, **PPPBP-NEt$_2$[13]** was synthesized (see Figure 2-10). The boronic ester of biphenyl was coupled with **DBNEt** using the polymerization conditions determined for **PPP-NEt$_2$(dppf)[12]** [$PdCl_2$(dppf), DMF/H_2O, and $NaHCO_3$]. During the course of the polymerization, it was noted that the polymeric / oligomeric materials being formed were precipitating out of solution much earlier than for the **PPP-NEt$_2$** reactions. Subsequent workup revealed only low molecular weight components ($\overline{M}_n$ < 5000 g/mol) for the isolated polymer as determined by GPC versus polystyrene standards and a high level (1.21%) of bromine endgroups as detected by elemental analysis. Only 51% of a tan material was recovered indicating that the precipitating oligomers are causing an imbalance in the functional groups present in solution. Without a proper balance of reactive endgroups in step growth polymerizations, chains will be prevented from growing into high molecular weight polymers. Insolubility was quickly reached in the growing **PPPBP-NEt$_2$[13]** system, as evidenced by early polymer precipitation from the reaction media.

The low molecular weight and solubility problems of the **PPPBP-NEt$_2$[13]** system naturally led to the swinging of the experimental pendulum back to more substituted phenylene systems. A polymer with every phenylene ring substituted with an alkoxy-amine side chain should be more soluble during the polymerization and the subsequent quaternized polymer more water soluble. Figure 2-13 shows two reagents that could be used in a Suzuki polymerization to achieve the maximum substituted PPP. The synthesis of compounds **17** and **18** was attempted by the reaction of **DBNEt** with magnesium turnings or n-butyllithium followed by quenching with trimethyl borate

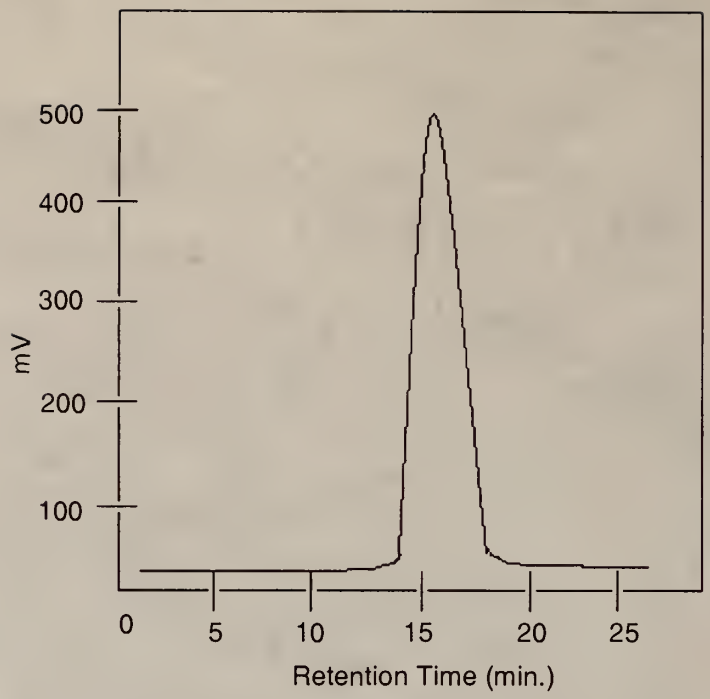


Figure 2-12. Gel permeation chromatogram for **PPP-NEt$_2$(dppf)[12]**.

Table 2-1. Catalyst effect on the molecular weight properties of PPP-NEt$_2$ polymers.

catalyst	reaction solvent	yield	Calibration method	$\overline{M}_n$ kg mol^{-1}	MP kg mol^{-1}	$\overline{M}_w$ kg mol^{-1}	$\overline{M}_w/\overline{M}_n$
Pd(OAc)$_2$	THF	38%	PS	5.0	4.8	19.5	3.91
			PPP[a]	3.9	3.8	12.9	3.29
Pd(OAc)$_2$	DMF	76%	PS	**15.9**	24.3	35.0	**2.20**
			PPP	10.8	15.6	21.5	1.99
PdCl$_2$(dppf)	THF	95%	PS	**18.7**	19.4	22.1	**1.18**
			PPP	12.4	12.8	14.4	1.16
Pd(OAc)$_2$	acetone	92%	PS	12.6	21.4	28.6	2.27
			PPP	8.8	14.0	18.0	2.05

GPC results in $CHCl_3$ vs. polystyrene standards.
$Pd(OAc)_2$ data taken from Dr. Peter Balanda dissertation U. of Florida.
[a] Universal calibration using values derived for PPP in THF.

Table 2-2. Elemental Analysis results for PPP monomers and polymers.

Species		%C	%H	%N	%I	%Br	Anal. Calcd. for
DINEt	Theo.	38.59	5.40	5.00	45.30	-	$C_{18}H_{30}N_2O_2I_2$
	Exp.	38.81	5.53	4.90	-	-	
DBNEt	Theo.	41.00	5.41	6.83	-	34.33	$C_{14}H_{22}N_2O_2Br_2$
	Exp.	41.13	5.44	6.71	-	-	
PPPmodel (10)	Theo.	78.21	8.76	6.08	-	-	$C_{30}H_{40}N_2O_2$
	Exp.	78.41	9.56	5.90	-	-	
PPPmodel+ (11)	Theo.	60.34	7.45	4.14	-	23.34	$C_{34}H_{50}N_2O_2Br_2$
	Exp.	61.27	7.67	4.29	-	22.54	
PPP-NEt_2 (dppf)[12]	Theo	74.95	8.91	7.28	-	-	$C_{24}H_{34}N_2O_2Br_{0.026}$
	Exp.	75.21	8.94	8.01	-	0.45	
PPP-NEt_2 (Br-72)[14]	Theo.	74.95	8.91	7.28	-	0.53	$C_{24}H_{34}N_2O_2Br_{0.026}$
	Exp.	75.09	8.92	8.05	-	0.54	
PPP-NEt_2 (I-3)[15]	Theo.	74.28	8.77	7.22	1.47	-	$C_{24}H_{34}N_2O_2I_{0.045}$
	Exp.	67.32	8.42	6.01	1.48	-	
PPP-NEt_2 (I-24)[16]	Theo.	74.82	8.83	7.27	0.76	-	$C_{24}H_{34}N_2O_2I_{0.023}$
	Exp.	71.85	8.45	6.78	0.77	-	
PPPBP-NEt_2[13]	Theo.	78.60	8.30	6.11	-	-	$C_{30}H_{38}N_2O_2$
	Exp.	70.25	8.22	5.75	-	1.21	
PPP-NEt_3+ [19]	Theo.	54.02	7.85	4.63	-	21.48	$C_{24}H_{34}N_2O_2$ · 1.6 C_2H_5Br · 2.54 H_2O
	Exp.	52.35	7.61	4.31	-	21.40	
PPPBP-NEt_3+ [20]	Theo.	60.27	7.09	8.05	-	23.63	$C_{34}H_{48}N_2O_2Br_2$
	Exp.	65.68	8.05	5.35	-	11.98	

Table 2-3. Effect of DBNEt or DINEt on the molecular weight of PPP-NEt_2 polymers.

polymer	reaction solvent	reaction type	reaction time (hours)	$\overline{M}_n$	MP	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
PPP-NEt_2 (Br-72)[14]	DMF/H_2O	Suzuki	72	15.9	24.3	35.0	2.20
PPP-NEt_2 (I-3)[15]	DMF/H_2O	Suzuki	3	10.9	13.3	16.6	1.52
PPP-NEt_2 (I-24)[16]	DMF/H_2O	Suzuki	24	15.3	19.5	27.5	1.80

Molecular weight values are expressed in units of kg mol^{-1}.
GPC relative to polystyrene standards.

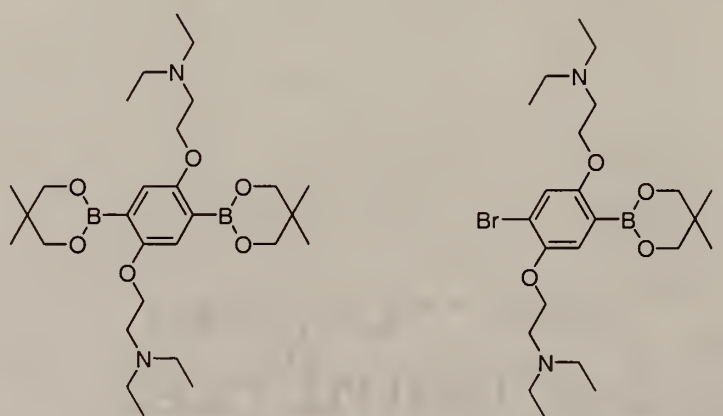


Figure 2-13. Envisioned boronic reagents for a more substituted PPP-NEt_2 polymer.

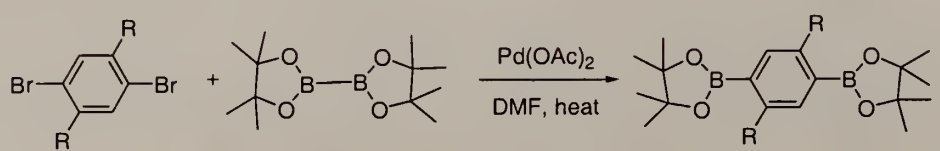


Figure 2-14. Pd catalyzed coupling to diboronic reagents for Suzuki couplings.

and transesterification with neopentyl glycol. Both attempts were unsuccessful, possibly caused by an interaction of the amine groups to the trimethyl borate hindering formation of the new phenyl-boron bond. Grignard and lithiation procedures were effective as evidenced by a substantial amount of dehalogenated material in the crude isolated material. Future work could explore using a palladium catalyzed reaction between di-halogenated phenylene's and diboron pinacol ester (see Figure 2-14) that has been shown to effectively produce boronic reagents for Suzuki reactions[70] as an alternative route to the desired compound **18**.

Polymer Quaternization

Quaternization of the amine sites followed preparation of the neutral polymers. Synthesis of poly[2,5-bis(2-{*N,N,N*-triethylammonium}-1-oxapropyl)-1,4-phenylene-*alt*-1,4-phenylene] dibromide (**PPP-NEt$_3$+[19]**) is accomplished by heating the neutral polymer in a DMSO / THF solution with bromoethane for 3 days (Figure 2-15). ^{1}H-NMR indicates that a high degree of the amine sites are quaternized (~90%). Elemental analysis for bromine content also reflects 90% quaternization (see Table 2-2). The beauty of synthesizing the neutral polymer first is in the ease of traditional polymer analyses that can be performed. Analysis of charged polyelectrolytes can be a rigorous and difficult undertaking,especially with GPC due to aggregation and charge interaction with the column material. Assuming the methods used to quaternize the amine sites are gentle enough not to break bonds along the PPP backbone or cleave side chains, molecular weight data corresponding to the neutral polymer should be a good reflection of the molecular weight of the water soluble version. **PPP-NEt$_3$+[19]** displayed excellent solubility in both acidic and neutral aqueous media. Solutions were stable over the time

frame of days with only minimal precipitation of polymer from solution observed on samples stored over a month.

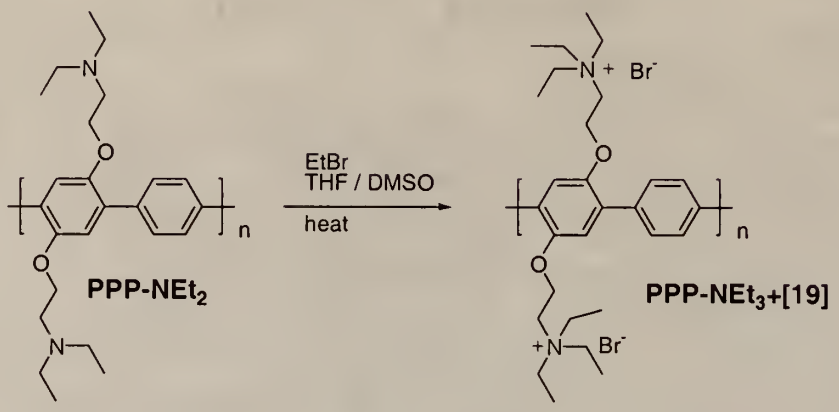


Figure 2-15. Quaternization of PPP-NEt_2.

PPPBP-NEt_2[13] was subjected to the same quaternization conditions as shown in Figure 2-15. Complete quaternization of this material was not achieved as the neutral material was difficult to dissolve in the quaternization media. ^1H NMR analysis of the material was unsuccessful due to the poor solubility in common deuterated solvents. Elemental analysis (Table 2-2) of the oligomers revealed a 11.98 weight percent of bromine. Of this amount 10.77% of bromine is due to quaternized ammonium sites and 1.21% is inherent from the parent **PPPBP-NEt_2[13]**. Full quaternization of all amine sites would require 23.63% bromine. Overall, this indicates that approximately half of the amine sites were quaternized. The resulting quaternized oligomers were no longer soluble in $CHCl_3$ or THF, but had reasonable solubility on the order of 5×10^{-3} M (based on repeat unit MW) in warm acetonitrile or DMSO. Cloudy "suspensions" in neutral H_2O were formed in the 10^{-3} M concentration range. The polymer was soluble in water only if the pH was lowered to around 2 or 3.

Physical Properties of PPP Type Polymers

For optical display uses, such as organic light emitting devices (OLED's) envisioned for **PPP-NEt$_3$+[19],** the two most important physical properties for the polymer are absorption and emission wavelengths and thermal stability. The absorption and emission wavelengths will obviously control the color of the display device and LED's operating under a high bias are limited in lifetime by thermal and electric field induced degradations. Materials with low barriers to thermal degradation are of limited use.

The solution absorbance and emission behavior of the newest **PPP-NEt$_2$[12]** and **PPP-NEt$_3$+[19]** samples match the data reported for the initial polymer samples prepared by Dr. Peter Balanda. Absorption spectra for the neutral polymer in THF (plot c), neutral polymer in 1M HCl (plot b) and quaternized polymer in H_2O (plot a) are represented on the left half of the graph in Figure 2-16. Interestingly, a significant blue shifting of the solution absorption maximum occurs from the neutral (λ_{max} = 350 nm) to quaternized (λ_{max} = 330 nm) polymer. In theory, the charges formed on the amine sites along the backbone of the PPP polymer should repel other polymer chains and each other on the same chain, stiffening each chain. This new state of the polymer should reduce steric interactions and red shift the absorbance to lower energy. If this red shifting is occurring, it is overcome by the additional effect of creating very specific point charges in space along the backbone which in turn have their own effect on the absorption pushing it into higher energy levels.

The solution emission results are plotted on the right half of Figure 2-16 and are shown on a log scale to allow a comparison of the large differences in intensity of

emission between the neutral polymer in THF (plot f), neutral polymer in 1M HCl (plot d), and the quaternized polymer in H_2O (plot e). Each polymer has a brilliant blue solution and thin film luminescence with an emission maximum wavelength of ca. 410 nm in THF and water. Intensity of luminescence increases 4 orders of magnitude in the quaternized **PPP-NEt$_3$+[19]** over the neutral polymer. This is attributed to the quenching of the excited state by the lone pair of electrons on the nitrogen sites in the neutral polymer. Quaternization prevents this quenching mechanism. Figure 2-17 shows the emission results on a linear intensity scale normalized to 1 for the neutral polymer, **PPP-NEt$_2$[12]**. When the plot is viewed in this scaling, it is easily seen that the line shape of emission is typical of photoluminescent polymers in solution with a broad peak and small shoulder that tails into higher wavelength regions.

It was theorized that the **PPPBP-NEt$_2$[13]** would have fewer side chain to backbone interactions than **PPP-NEt$_2$[12]** and thus a λ_{max} at higher wavelength. Optical absorbance and emission in solution was identical to that of the higher molecular weight **PPP-NEt$_2$[12]** samples. UV-Vis absorption measurements were taken on thin films cast from THF of both **PPPBP-NEt$_2$[13]** and **PPP-NEt$_2$[12]**. The plots were nearly identical with an absorption maximum just above 350 nm. If we assume that the oligomeric **PPPBP-NEt$_2$[13]** has reached a degree of polymerization such that its maximum absorption wavelength has been achieved (typically this would be 12-15 rings or only a degree of polymerization of 4 in this case), the similarity in thin film absorption data indicates that the alkoxyamine side groups along the backbone of **PPP-NEt$_2$[12]** are disturbing the conjugated backbone planarity very little, allowing the conjugated backbone to maintain a very rigid conformation.

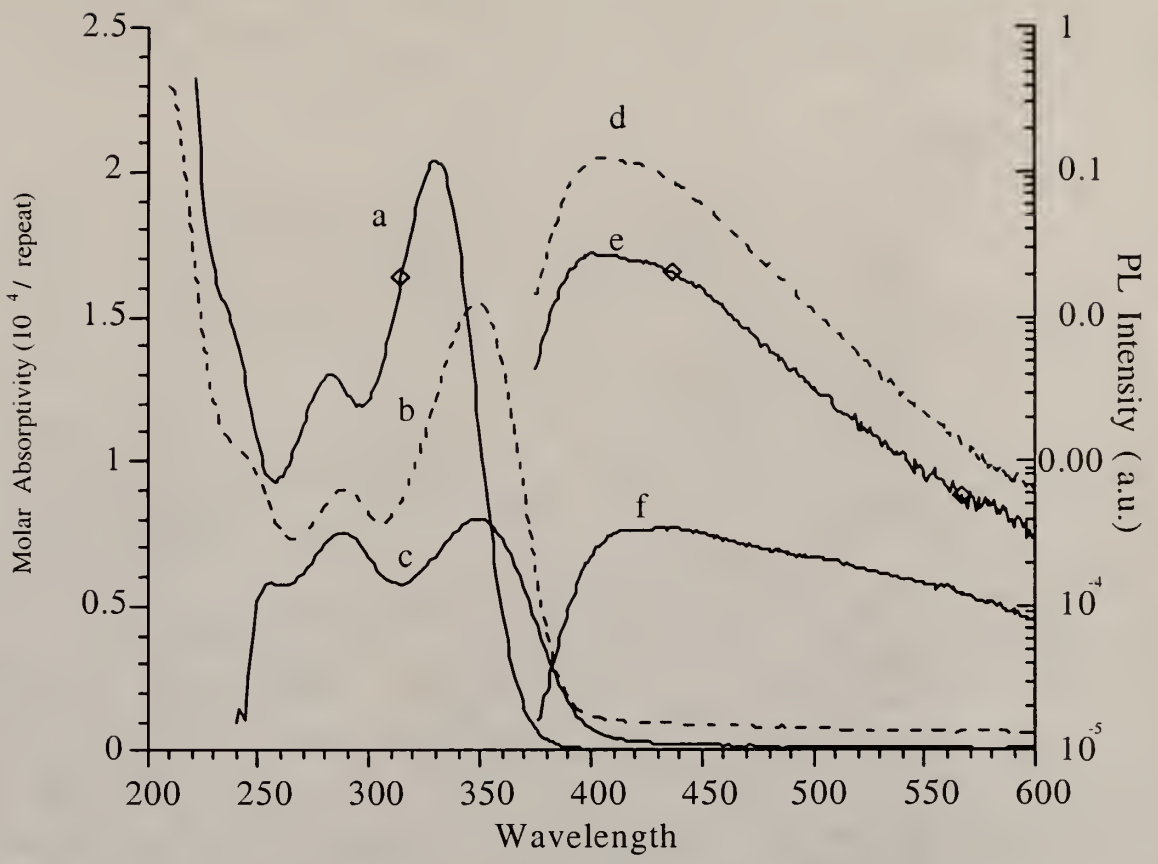


Figure 2-16. UV-Vis / Emission behavior of neutral and water soluble PPP-NEt.
a) PPP-NEt_2[**12**] in THF: plots c and f
b) PPP-NEt_2[**12**] in 1 M HCl: plots b and d
c) PPP-NEt_3+[**19**] in H_2O: plots a and e
Figure taken from Balanda, P.B.; Ramey, M.B.; Reynolds, J.R. *Macromolecules* **1999**, *32*, 3970.

Thermal analysis by TGA (under nitrogen atmosphere) (Figure 2-18) indicated an onset for decomposition over 300°C for **PPP-NEt_2[12]** and at *ca.* 230°C for **PPP-NEt_3+[19]** (with a small amount of water loss at lower temperatures). From the perspective of device applications, the most important degradation event is the one which occurs first. The first degradation event for both polymers was determined to be side chain cleavage, including the loss of ethyl bromide for the quaternized sample. The

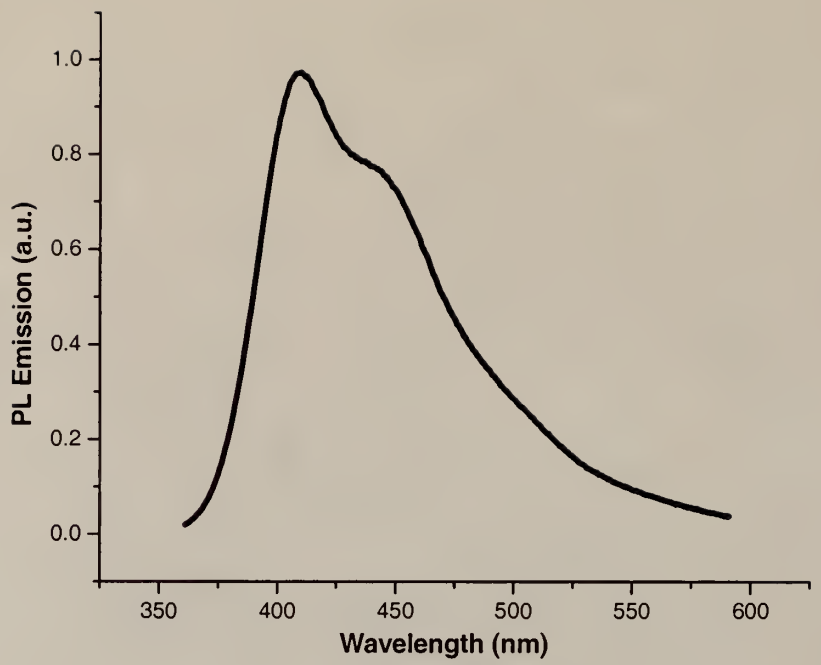


Figure 2-17. Photoluminescent spectrum of **PPP-NEt$_2$[12]** in THF with normalized and linear emission scale.

fact that the thermal degradation of these alkoxy substituted PPP's is a relatively clean process may provide a route to hydroxylated PPP's. Samples of **PPP-NEt$_2$[12]** heated to 300^0 for 10 min were no longer soluble in $CHCl_3$ or THF, but did possess blue photoluminescence when exposed to ultraviolet light. Treatment of **PPP-NEt$_2$[12]** with BBr_3 (a reagent known for its ability to cleave aryl ethers) also resulted in a material insoluble in $CHCl_3$ or THF with the above mentioned emission characteristic.

Conclusions

An interesting water soluble poly(*p*-phenylene) (**PPP-NEt$_3$+[19]**) has been synthesized by a variety of modifications of Suzuki polymerization techniques. The use

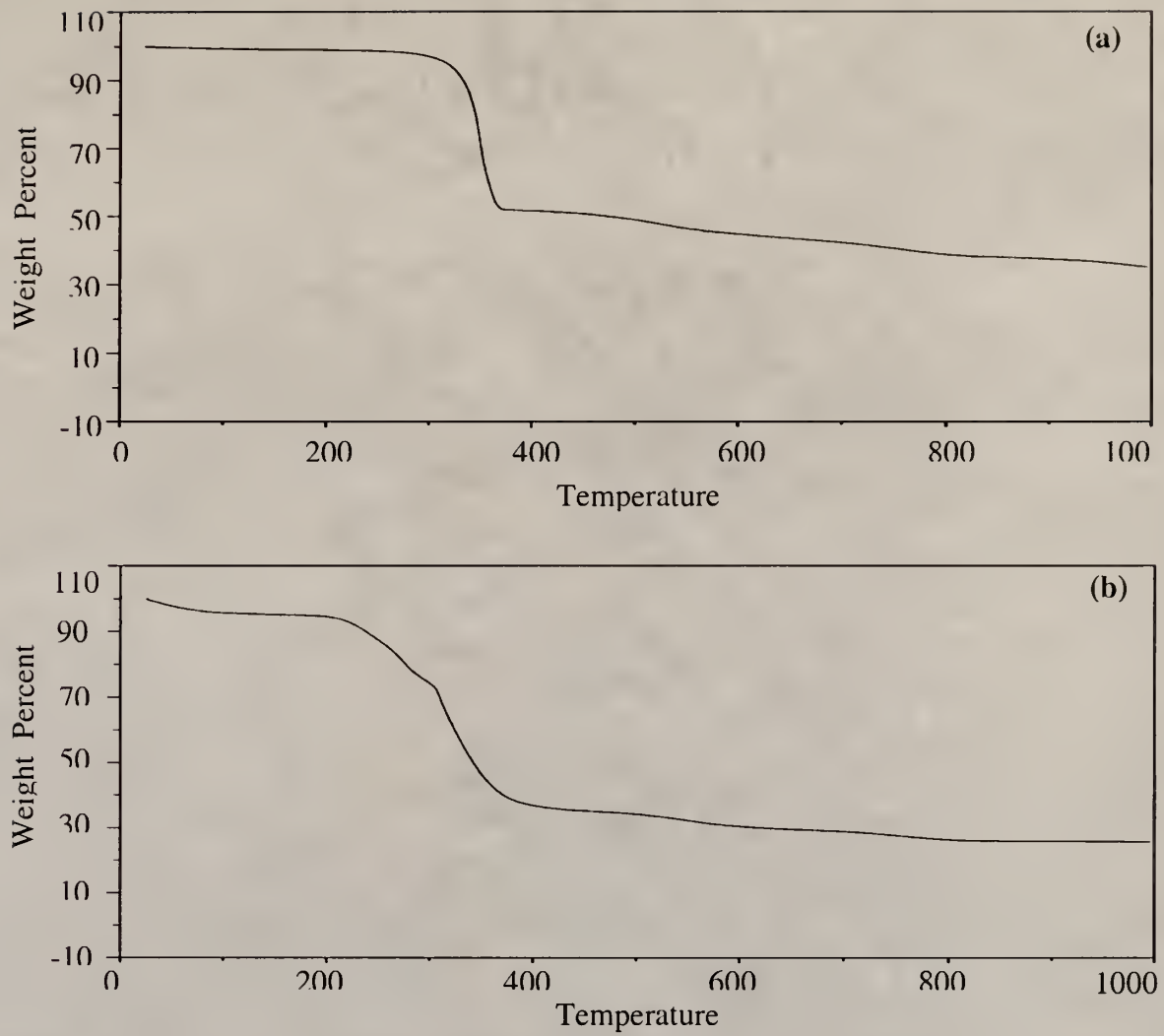


Figure 2-18. TGA thermograms for neutral and water soluble PPP-NEt under N_2.
a) PPP-NEt_2[**12**]
b) PPP-NEt_3+[**19**]

of $PdCl_2$(dppf) as catalyst has increased synthetic yield to the point whereby a relatively high molecular weight polymer with low polydispersity can be made without the extra steps of "cleaning" precipitated Pd out of the polymer. The $PdCl_2$(dppf) catalyst was also successful in allowing polymerization scale-up to the multi-gram level. For this system, maximum chain growth is limited by the precipitation of longer polymer chains during the coarse of the reaction.

Increasing the number of unsubstituted phenyl rings in the polymer backbone, **PPPBP-NEt$_2$[13]**, lowers molecular weight due to precipitation of the polymer out of the reaction prior to high conversions. Subsequent optical absorption data on thin film castings of less substituted samples to the more substituted **PPP-NEt$_2$[12]** helps support the theory that the alkoxyamine side groups on **PPP-NEt$_2$[12]** have minimal interactions that affect backbone planarity.

CHAPTER 3
CATIONIC POLY(*p*-PHENYLENE-*co*-THIOPHENE)'s

Introduction

While poly(*p*-phenylene)'s such as **PPP-NEt$_3$+[19]** are typically strong blue-emitting polymers, it is desirable to have structurally similar materials with a range of emission wavelengths. One approach to "tune" the emission wavelength of a polymer is to chemically change the makeup of the backbone structure. By incorporation of more electron rich moieties into the repeat unit structure, the highest occupied molecular orbital (HOMO) to lowest occupied molecular orbital (LUMO) electronic bandgap is lowered. Specifically, electron rich species raise the HOMO and have little effect on the LUMO, thereby decreasing bandgap overall. As the bandgap is lowered, the energy needed to excite an electron into the LUMO is reduced and therefore the energy (wavelength) of light emitted upon relaxation will be of lower energy. For a more complete description of light emission consult chapter 1 of this dissertation.

Inclusion of heterocycles, such as thiophene, furan, and pyrrole into co-polymers with PPP attract much attention due to the substitution possibilities on phenylene rings and the bandgap reduction due to a greater tendency towards planarity and electron richness of the heterocycle. The original work to be discussed in this chapter will use the incorporation of thiophene into the backbone of an alternating substituted phenylene-*co*-thiophene polymer to create a water soluble polymer that emits at higher wavelengths than the "parent" **PPP-NEt$_3$+[19]** polymer discussed in Chapter 2 of this dissertation.

Early Synthetic Attempts

An early approach to incorporate thiophene units into a poly(*p*-phenylene-*co*-thiophene) backbone was based on a poly(1,4-diketone) prepared by a Stetter reaction that was treated with Lawesson's reagent to incorporate sulfur into the backbone (Figure 3-1a).[71] The harsh conditions required was a major flaw in this approach, as crosslinking was promoted. Czerwinski et al. used a Grignard coupling between *p*-dibromobenzene and 2,5-dibromothiophene in various feed ratios to incorporate thiophene and phenylene units into the backbone (Figure 3-1b).[72] Alternating copolymers containing arylene and bithiophene repeat units have been synthesized via electrochemical polymerization of 1,4-di-2-thienylarylenes (Figure 3-1c).[73] The electrochemical polymerizations form insoluble films on conductive substrates limiting polymer processing to the initial deposition. Pelter et al. used zinc chloride to metalate the 5 and 5' positions of 1,4-di-(2-thienyl)phenylene and reacted the intermediate with 1,4-dibromo-2,5-disubstituted benzenes via a Grignard coupling (Figure 3-1d).[74] The polymers could be doped by ferric chloride or iodine to conductivities between 10^{-5} and 10^{-3} Ω^{-1} cm^{-1}.

Dr. Luping Yu and co-workers first report the synthesis of an alternating poly(*p*-phenylene-*co*-thiophene) by a Stille coupling polymerization in 1993.[75] The Stille reaction offers much more flexibility in the selection of monomers and reaction conditions than many of the pathways shown in Figure 3-1. Figure 3-2 shows a general polymerization scheme for a Stille type polymerization. In this case, 1,4-diiodo-2,5-dialkoxybenzenes were reacted with 2,5-bis(tributylstannyl)thiophene. The polymers were analyzed via gel permeation chromatography revealing a number average molecular

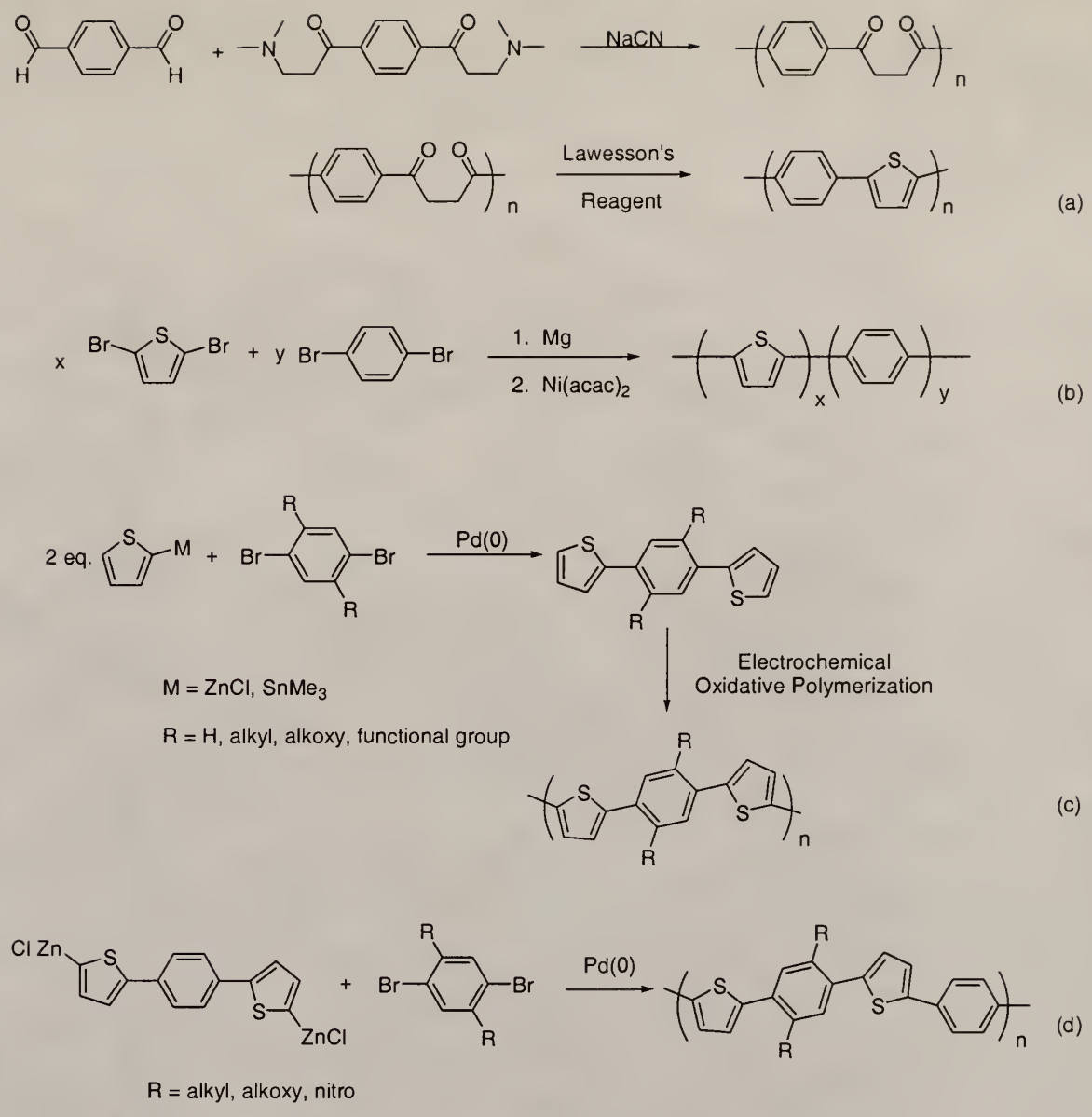


Figure 3-1. Literature examples of phenylene-*co*-thiophene type polymers.

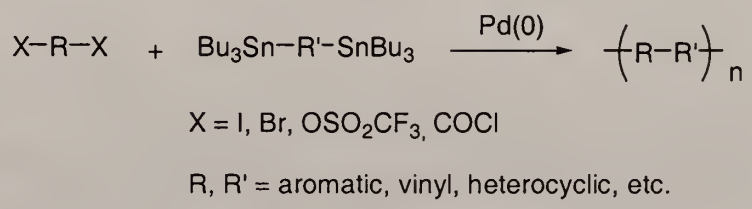


Figure 3-2. General scheme for the Stille polymerization.

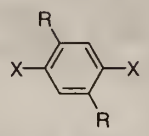
weight of ca. 14,000 g mol^{-1} versus polystyrene standards. This class of polymer possesses a bandgap of ca. 2.4 eV (520 nm), falling between that of poly(*p*-phenylene), 3.0 eV (413 nm), and polythiophene, 2.1 eV (590 nm).[76] An emission at 525 nm was present in photoluminescence studies conducted in THF when the polymer solution was excited with a wavelength of light corresponding to its absorption maximum when the polymer solution was excited with a wavelength of light corresponding to its absorption maximum.

Optimization of the Stille Coupling Polymerization

In order to maximize the efficacy of the Stille reaction for polymerizations, a more detailed study by Yu et al. was conducted in 1995 to examine monomer, catalyst, and solvent effects on the molecular weight of a variety of conjugated polymers.[77] The organohalides and triflates shown in Table 3-1 and the organotin monomers shown in Table 3-2 were combined under a variety of conditions in the presence of palladium catalysts. Polymer repeat unit structures are given in Figure 3-3.

Several general conclusions could be made from the polymers synthesized from the different combinations of monomers and reaction conditions. Diiodo-substituted monomers are more reactive than dibromo-substituted monomers. Dialkyl-substituted phenylene monomers gave higher molecular weights than the more electron rich dialkoxy-substituted phenylene monomers. The oxidative addition step in a palladium catalyzed reaction is usually facilitated by electron withdrawing or less electron donating groups. PPP type polymerizations were found to be poor in all cases with dimeric or trimeric species formed. In general, the organotin monomer prefers to be electron rich and the organohalide (or triflate) to be electron deficient.

Table 3-1. Structures of the organohalides and triflates for the Stille reactions.

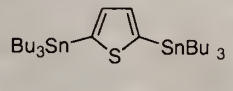


1-8

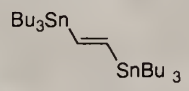
Compound	R	X
1	OC_8H_{17}	I
2	OC_8H_{17}	Br
3	OC_8H_{17}	OTf
4	C_8H_{17}	I
5	C_8H_{17}	Br
6	C_8H_{17}	OTf
7	$OC_{11}H_{23}$	OTf
8	no substitution	OTf

*Taken from Bao, Z.; Waikin, C.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 12426.

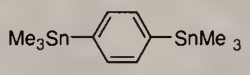
Table 3-2. Structures of the organotin monomers for the Stille reactions.



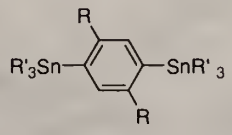
9



10



11



12 - 14

Compound	R	R'
12	OCH_3	CH_3
13	OCH_3	n-C_4H_9
14	OC_7H_{15}	CH_3

*Taken from Bao, Z.; Waikin, C.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 12426.

Typically 2 mol% catalyst was used as higher loadings of catalyst lowered molecular weight. Adjustment of the 1:1 organohalide to organotin reactant equivalent

ratio to account for reduction of the palladium (II) catalyst to the active palladium (0) species by the organotin species increased molecular weights. The organotin compound would be used in a 1.02 equivalent amount compared to 1.00 equivalent of organohalide.

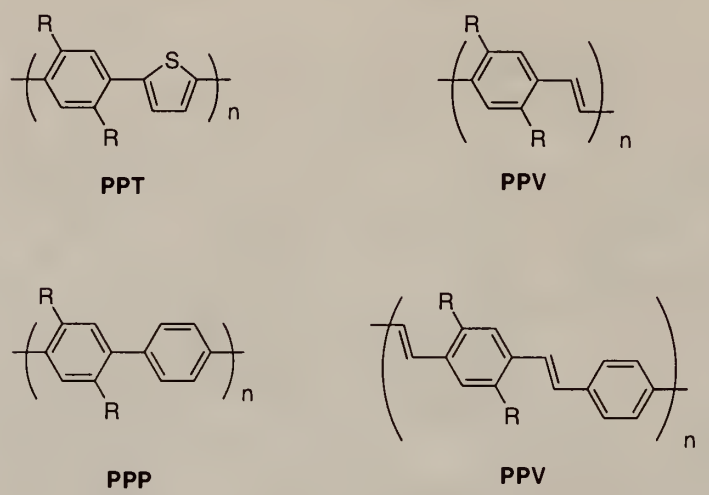


Figure 3-3. Representative polymer repeat units of Stille polymerizations.
$R = C_nH_{2n+1}$ or OC_nH_{2n+1}
Taken from Bao, Z.; Waikin, C.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 12426.

Ability of the solvent to both solubilize the coupled species and stabilize the catalyst is of utmost importance in the Stille reaction and becomes an even more important issue when addressing conjugated polymers and their inherent solubility problems.[78] Common solvents for the Stille reaction include THF, toluene, and DMF. DMF is known to accelerate the palladium-catalyzed reactions by acting as a ligand to the palladium center.[79] In the case of the PPT polymers synthesized above, it was found that DMF did accelerate the polymerization, however, the growing polymers were not sufficiently soluble to remain in solution sufficiently long enough to achieve higher molecular weights. THF was able to solubilize the polymer and stabilize the catalyst for reaction times up to 7 days.

Number average molecular weights of up to 22,000 g mol^{-1} were achieved for the PPT polymers using 1.00 equivalent of 1,4-diiodo-2,5-dioctylbenzene, 1.02 equivalents of 2,5-bis(tributylstannyl)thiophene, and 2 mol% $PdCl_2(PPh_3)_2$ catalyst in 80 ^{0}C DMF for one week. Of all organotin monomers studied, the 2,5-bis(tributylstannyl)thiophene (see Table 3-2) was the most reactive, as the electron donating property of the sulfur atom may accelerate the transmetalation step which has been proposed to be the rate determining step for palladium-catalyzed cross coupling reactions.[80] An alternate tin reagent not used in Yu's study is 2,5-bis(trimethylstannyl)thiophene, which is a more "friendly" reagent in that it is a solid at room temperature allowing for purification by recrystallization. The distillation techniques needed to purify 2,5-bis(tributylstannyl)thiophene are difficult and workers may be exposed to alkyltin vapors, which are very toxic. One drawback to the use of 2,5-bis(trimethylstannyl)thiophene is the transfer of a methyl group during coupling instead of the desired thiophene group and limiting chain lengths in polymerizations.

This methodology appeared attractive for coupling distannylated thiophene with 2,5-bis(3-[*N,N*-diethylamino]-1-oxapropyl)-1,4-diiodobenzene (**DINEt**)[see Chapter 2]. If successful, a neutral poly(*p*-phenylene-*co*-thiophene) with alkoxyamine side chains on the phenylene units would be created that should become water soluble upon treatment with ethyl bromide. The solution emission of this polymer should fall in the green to yellow visible wavelength range by comparison to literature values. Using the insights into the Stille coupling found by Yu and coworkers, and taking into account the specific differences between the proposed system and the literature examples, a systematic approach was designed to maximize the molecular weight of poly({2,5-bis[2-(*N,N*-

diethylamino)-1-oxapropyl]-1,4-phenylene}-*alt*-2,5-thienylene) (**PPT-NEt_2**) which is easily converted to the quaternary ammonium salt, poly{2,5-bis[2-(*N,N,N*-triethylammonium)-1-oxapropyl]-1,4-phenylene-*alt*-2,5-thienylene} dibromide (**PPT-NEt_3+).** It was also desired to determine if a Suzuki type polymerization would work using thiophene diboronic reagents. A Suzuki approach would allow for the use of much less toxic boronic reagents than the tin reagents used in Stille couplings. The results and discussion following will address these aspects in greater detail.

Results and Discussion

Monomer Syntheses and Suzuki Coupling Test Reactions

In order to effectively synthesize PPT-NEt_3+ of high molecular weight via a Stille or Suzuki polymerization, 2,5-bis(3-[*N,N*-diethylamino]-1-oxapropyl)-1,4-diiodobenzene (**DINEt**) (Figure 2-7) and 2,5-bis(trimethylstannyl)thiophene (**21**) or 2,5-thiophene diboronic acid (**22**) as co-monomers were selected. Literature precedent for Suzuki polymerizations involving thiophene were not present, but success of this type of polymerization was desired because the aryl tin reagents used in the Stille reaction are somewhat less reactive as compared to the aryl boronic acids used in the Suzuki coupling. A diiodobenzene monomer was chosen over a dibromo reagent due to its higher reactivity in Pd coupling reactions. Particular attention was paid to the stringent monomer purification requirements needed for complete conversion of functional groups.

The synthesis of 2,5-bis(trimethylstannyl)thiophene (**21**) by literature methodology is outlined in Figure 3-4.[81] Thiophene was treated with 2.05 equivalents of *n*-butyllithium and refluxed in a hexane / TMEDA solution for 30 minutes, cooled to 0 ^{0}C in an ice bath, and quenched with 2.05 equivalents of trimethylstannyl chloride. After

stirring overnight, aqueous extraction, followed by removal of hexane under reduced pressure revealed a slightly brown solid. The stannylated compound was distilled under vacuum, and recrystallized twice from pentane to yield white crystals in 69% yield.

The corresponding Suzuki reagent, 2,5-thiophene diboronic acid (**22**) was prepared by treating 2,5-dibromothiophene with 2.2 equivalents of Mg, followed by quenching with an excess of dry trimethylborate. The reaction was stirred overnight and 1M HCl was added to protonate the di-acid and dissolve all magnesium salts. After an aqueous/ Et_2O extraction, the crude product was precipitated into 1M HCl, collected, and recrystallized from hot H_2O. A 40% yield of white crystals was recovered and dried *in vacuo* at 100 ^{0}C for 3 hours. As is the case with boronic acids, purification and drying were simplified by reacting the di-acid with neopentyl glycol in refluxing benzene in a transesterification manner to produce the 2,5-thiophene diboronate ester (**23**) as white crystals in 70% yield as outlined in Figure 3-5.

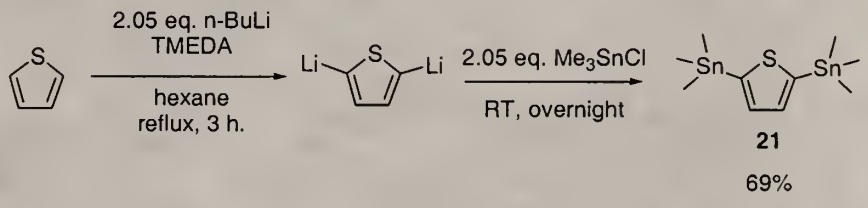


Figure 3-4. Synthesis of 2,5-bis(trimethylstannyl)thiophene.

Due to the lack of literature attempts at polymerizing a thiophene di-boronic acid or ester, a test coupling procedure was carried out to determine if the reagent would couple before degradation. A simple three component ring system was chosen instead of test polymerizations for the study, since too many factors are present in polymerizations

that may deter the reaction. Figure 3-6 shows the general Suzuki coupling reaction employed to check reaction parameters. A variety of conditions were used to couple compound **23** and 4-bromotoluene. 4-bromotoluene was chosen over 4-iodotoluene because of its lowered reactivity. In essence, if conditions are found to allow the coupling to occur with bromo-reagents, iodo-reagents should perform better under the same conditions and oftentimes the reactivity of bromo-compounds is sufficient for use in Suzuki couplings eliminating the need for the more expensive iodine compounds. Sodium bicarbonate ($NaHCO_3$) and $PdCl_2$(dppf) (1 mol%) were used as base and catalyst, respectively, in all test reactions. Solvents were varied between THF, DMF, and toluene, along with adjusting the reaction temperature from reflux to room temperature. In all cases a mixed 5:1 ratio of the organic solvent to water was used to promote formation of the more reactive boronate anion. To account for the high reactivity the thiophene diboronate ester, reactions were conducted via one pot or the diboronate ester was added slowly in a solution of solvent from an addition funnel.

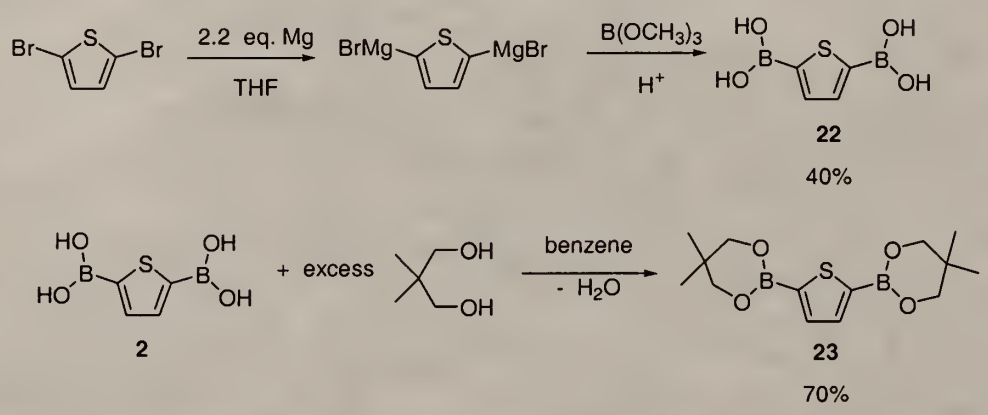


Figure 3-5. Synthesis of 2,5-thiophene diboronate ester.

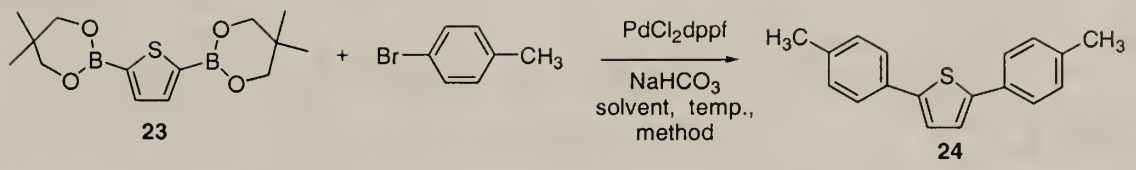


Figure 3-6. Test coupling reaction of 2,5-thiophene diboronate ester and 4-bromotoluene.

Test reactions were monitored by thin layer chromatography to check for the consumption of molecule **23** and 4-bromotoluene along with the appearance of new compound spots. Reactions which displayed positive TLC results were worked up isolating the organic products. Subsequently, the material was analyzed by gas chromatography/mass spectrometry (GC/MS) to determine composition. Table 3-3 lists the various reaction combinations and results.

Surprisingly, coupling to any significant level does not occur in THF. Typically, even if THF proves to be a poor solvent for a Suzuki coupling, the reaction will proceed to the 20-30% range. GC/MS peaks were assignable only to the starting materials with a very small percent (<2%) of mono-substituted thiophene present upon slow addition of the boronate ester. It was hypothesized that THF may be degrading the reactive thiophene boronate ester. To help determine if this was the case, a small sample of compound **23** was placed in THF with catalyst and THF or DMF (and the correct ratio of water) without 4-bromotoluene and heated to 50 ^{0}C for 3 hours. The "reactions" were stopped and analyzed by GC/MS. Both revealed the peak assignable to compound **23** with no degradation products evident. From these results, it is evident that THF and DMF do not have any degradation effects on the boronate ester. The use of toluene as a higher boiling solvent did not promote the reaction and GC/MS revealed higher levels of degradation

products such as thiophene and its mono-boronate ester as a result of the higher temperatures.

Table 3-3. GC/MS results of Suzuki coupling of 2,5-thiophene diboronate ester and 4-bromotoluene.

Solvent	Temp	Catalyst	Method	Result
THF	RT	$PdCl_2dppf$	1 pot	SM
THF	reflux	$PdCl_2dppf$	1 pot	SM + degradation
Toluene	reflux	$PdCl_2dppf$	1 pot	SM + large degradation
THF	reflux	$PdCl_2dppf$	dropwise	low % mono
DMF	RT	$PdCl_2dppf$	1 pot	low % mono, SM
DMF	**72 ^{0}C**	$PdCl_2dppf$	**1 pot**	Product **24 , 75%**
DMF	**72 ^{0}C**	$PdCl_2dppf$	**dropwise**	Product **24 , 90%**
DMF	**72 ^{0}C**	**$Pd(OAc)_2$**	**dropwise**	Product **24 , 90%**

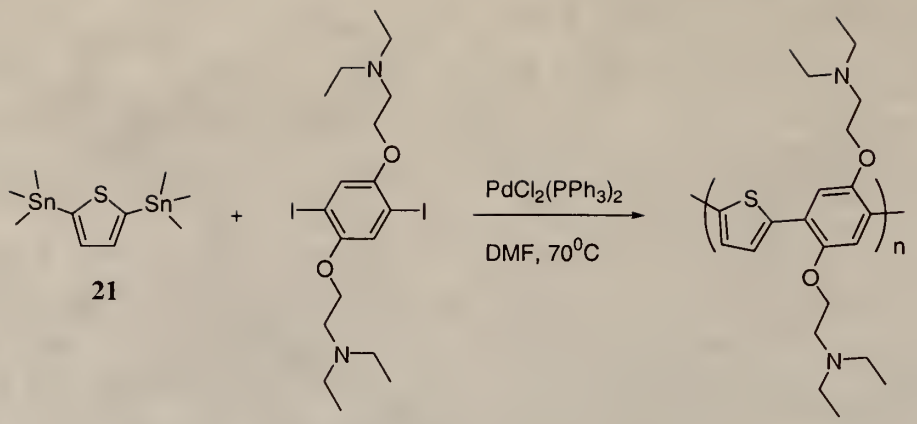
RT = Room Temperature (~22 ^{0}C)
SM = Starting Materials (Compound **23** and 4-bromotoluene)
Mono = One tolyl unit coupled to thiophene

The coupling was successful in all cases in which DMF at elevated temperatures was used. The ability of DMF to coordinate to the catalyst and increase catalytic activity is believed to account for the success of using this solvent in the reaction. GC/MS revealed good yields of product **24** for all DMF reactions at 72 ^{0}C, with excellent yields

for cases in which the boronate ester was added dropwise. As an additional test, the less reactive $Pd(OAc)_2$ catalyst was used and yields for the reaction were as high as those for the $PdCl_2$(dppf). The ability of $Pd(OAc)_2$ to be used in the coupling is important because the catalyst is one of the least expensive Pd catalysts. For polymerizations using compound **23**, the test reactions indicate that using DMF at 72 ^{0}C with one pot or dropwise addition of the boronate ester will be the best choice. These conditions will provide the best possibility for polymerization success with only inherent polymerization difficulties left to deter the reaction, such as solubility and complete conversion of functional groups before hydrolysis of the boronate ester from the thiophene.

Neutral Polymer Syntheses

Initial polymerizations were conducted using the Stille coupling route because of available guidelines in the literature for Stille couplings when used in thiophene polymerizations . The Stille coupling polymerization used in the synthesis of poly({2,5-bis[2-(*N,N*-diethylamino)-1-oxapropyl]-1,4-phenylene}-*alt*-2,5-thienylene) (**PPT-NEt$_2$**) is depicted in Figure 3-7. Gel permeation chromatography (GPC) and elemental analyses for the subsequent experiments described below are presented in Tables 3-4 and 3-5, respectively. It should be noted that the carbon analyses are significantly lower than what is expected which may be due to the fact that these highly aromatic polymers are difficult to combust and some carbonization may have occurred during the measurements. The iodine elemental analyses provide a rough method for approximating the degrees of polymerization. Not unexpectedly, attempts to synthesize **PPT-NEt$_2$** using the dibromobenzene derivative, **DBNEt**, were unsuccessful with only low molecular weight coupling products observed (results not shown).



21

DINEt

Polymer	Time	Method
PPT-NEt_2(48) [25]	48 h	1 pot
PPT-NEt_2(96) [26]	96 h	1 pot
PPT-NEt_2(240) [27]	240 h	1 pot
PPT-NEt_2(96-drop) [28]	96 h	dropwise

Figure 3-7. Stille coupling polymerization scheme for PPT-NEt_2.

Reactions were conducted under varied conditions to determine the optimal needed to achieve the highest molecular weight possible for **PPT-NEt_2**. The first set of reactions were carried out as one pot syntheses, where the stannylated compound, **DINEt,** and DMF were mixed together and heated to 70 ^{0}C. $PdCl_2(PPh_3)_2$ was then added in one portion in a catalytic amount to the reaction flask. **PPT-NEt_2(48)[25]** and **PPT-NEt_2(96)[26]** were synthesized with 48 and 96 hour reaction times followed by precipitation into MeOH. During the polymerization, polymer was seen to precipitate out and coat the reactor. **PPT-NEt_2(48)[25]** was collected in75% yield with a $\overline{M}_n$ of 3,200 g mol^{-1},while **PPT-NEt_2(96)[26]** was collected in 80% yield with a $\overline{M}_n$ of 4,100 g mol^{-1} (GPC versus PS standards)(see Table 3-2). Polydispersities of 1.7 were found for both, but with the extensive fractionation during purification this value is not indicative of the initial polymerization. Doubling the reaction time lead to a modest improvements in both

yield and $\overline{M}_n$, while increasing the reaction time to 10 days in **PPT-NEt$_2$(240)[27]** led to no appreciable molecular weight enhancement ($\overline{M}_n$ of 4,200 g mol^{-1}).

Later experiments were fine tuned to account for the possible degradation of the 2,5-bis(trimethylstannyl)thiophene when exposed to elevated temperatures in the reaction medium. **PPT-NEt$_2$(96-drop)[28]** was synthesized by slow dropwise addition of **21** to a solution of catalyst, **DINEt**, and DMF via an addition funnel over the course of 4 hours and allowed to run for 96 hours. The reaction was precipitated into MeOH, the crude polymer recovered by filtration, followed by extraction with MeOH and acetone for 24 hours each, and finally collected by extraction with chloroform (via Soxhlet extractor).

Table 3-4. Gel permeation chromatography results for Stille coupling of PPT-NEt$_2$.

polymer	reaction solvent	reaction type	reaction time (hours)	$\overline{M}_n$ kg mol^{-1}	*MP* kg mol^{-1}	$\overline{M}_w$ kg mol^{-1}	$\overline{M}_w/\overline{M}_n$
PPT-NEt$_2$ (48)[25]	DMF	Stille	48	3.2	4.3	5.2	1.70
PPT-NEt$_2$ (96)[26]	DMF	Stille	96	4.1	5.8	6.9	1.68
PPT-NEt$_2$ (240)[27]	DMF	Stille	240	4.2	5.4	7.2	1.71
PPT-NEt$_2$ (96-drop)[28]	DMF	Stille (dropwise)	96	5.3	6.9	9.0	1.70

GPC results in THF vs. polystyrene standards.

The chloroform soluble fraction constituted an 84% yield and ^{1}H and ^{13}C NMR analysis gave expected shift values with the proton peaks appearing as broad multiplets without defined splitting for all polymeric materials recovered (see Figure 3-8). This polymer exhibits a $\overline{M}_n$ of 5,300 g mol^{-1} (GPC versus PS standards). This methodology

Table 3-5. Elemental Analysis results for PPT monomers and polymers.

Species		%C	%H	%N	%I	%Br	Anal. Calcd. for
Compound 21	Theo.	29.32	4.92	-	-	-	$C_{10}H_{21}SSn_2$
	Exp.	29.65	4.60	-	-	-	
Compound 23	Theo.	54.52	7.20	-	-	-	$C_{14}H_{22}O_4B_2S$
	Exp.	54.70	7.14	-	-	-	
PPT-NEt_2 (48)[25]	Theo.	66.33	8.04	7.03	2.52	-	$C_{22}H_{32}N_2O_2SI_{0.079}$
	Exp.	65.23	7.84	6.65	2.50	-	
PPT-NEt_2 (96)[26]	Theo.	67.13	8.14	7.12	1.19	-	$C_{22}H_{32}N_2O_2SI_{0.037}$
	Exp.	63.64	8.03	6.46	1.20	-	
PPT-NEt_2 (240)[27]	Theo.	67.13	8.14	7.12	1.19	-	$C_{22}H_{32}N_2O_2SI_{0.037}$
	Exp.	63.99	7.99	6.60	1.22	-	
PPT-NEt_2 (96-drop)[28]	Theo.	67.38	8.17	7.15	0.97	-	$C_{22}H_{32}N_2O_2SI_{0.030}$
	Exp.	63.99	8.02	6.51	0.98	-	
PPT-NEt_3+ (96)[30]	Theo.	51.09	6.88	4.58	0.77	26.20	$C_{22}H_{32}N_2O_2SI_{0.037}$ · 2.0 C_2H_5Br
	Exp.	49.87	6.48	3.18	-	24.18	
PPT-NEt_3+ (96-drop)[31]	Theo.	51.16	6.89	4.59	0.62	26.24	$C_{22}H_{32}N_2O_2SI_{0.030}$ · 2.0 C_2H_5Br
	Exp.	49.73	6.52	3.29	-	23.62	
PPT-NEt_2 (Suz)[29]	Theo.	68.04	8.23	7.23	-	-	$C_{22}H_{32}N_2O_2S$
	Exp.	64.70	7.98	6.60	0.09	-	

produced a polymer with the lowest percent of halogentated endgroups(weight %I = 0.98; approximates a degree of polymerization = 27, corresponding to 54 rings) and highest

molecular weight by GPC of all trials. Slow addition of the more reactive tin compound allows for immediate coupling of the thiophene to **DINEt**. This limits the exposure of the stannylated compound to the elevated temperatures and lowers the chance of destroying the mass balance leading to end-capping of the polymer chains with thiophene or completely de-stannylating the thiophene. This method led to the highest degree of polymerization for the **PPT's** prepared.

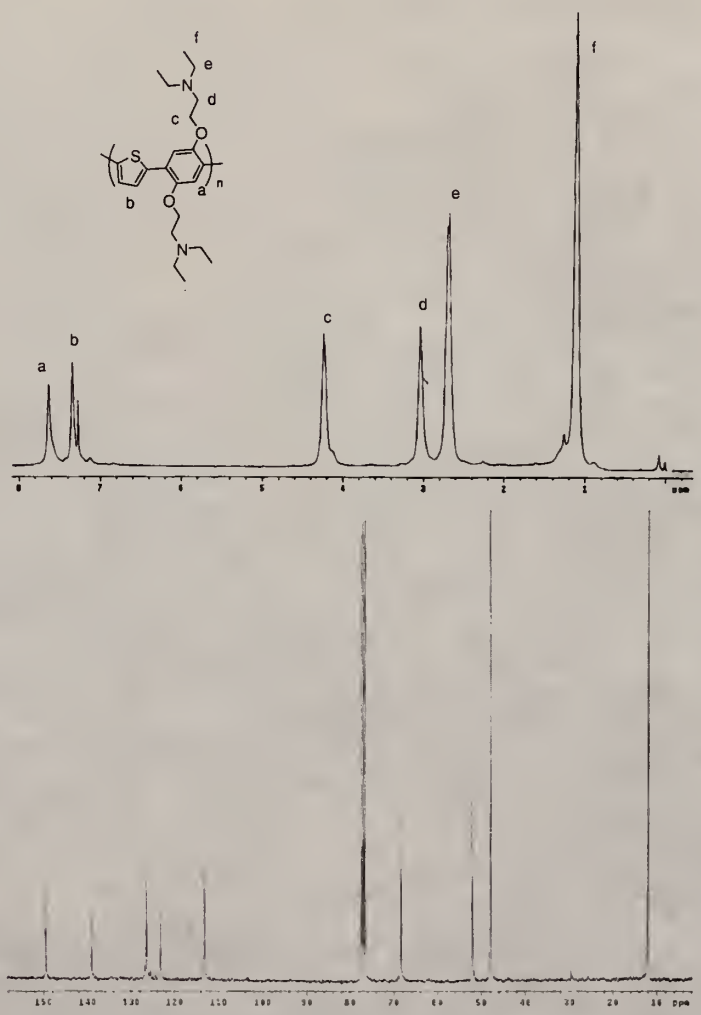


Figure 3-8. ^{1}H and ^{13}C NMR spectra of PPT-NEt_2[**28**].

The next synthetic progression after confirmation that a base set of **PPT-NEt$_2$** polymers had been created was to try the Suzuki coupling methodology as outlined in Figure 3-9. Compound **23** was added dropwise to a stirred solution of **DINEt**, $PdCl_2(dppf)$, and $NaHCO_3$ in a DMF / H_2O solvent solution at 70 ^{0}C. After 3 days, the reaction was precipitated into MeOH, the crude polymer recovered by filtration, followed by extraction with MeOH and acetone for 24 hours each, and finally collected by extraction with chloroform (via Soxhlet extractor). The material, **PPT-NEt$_2$(Suz)[29]**, was recovered in 50% yield.

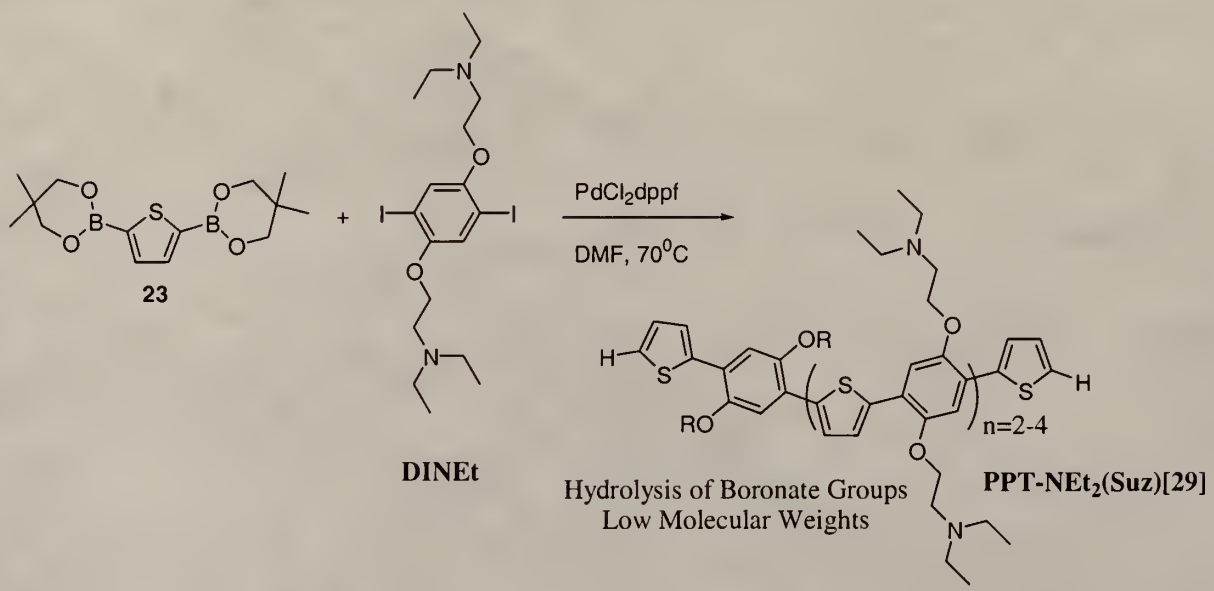


Figure 3-9. Synthesis of PPT-NEt$_2$[**29**] via Suzuki coupling polymerization.

Elemental analysis of the polymer (see Table 3-5) initially indicated a possible high molecular weight polymer with only 0.09 % by weight iodine found in the sample, however, GPC trials indicated very low molecular weight oligomeric species. UV-Vis absorption data showed a peak λ_{max} = 452 nm, some ten nanometers higher in wavelength than the well analyzed materials from the Stille polymerization (see Physical Properties

section). This evidence supports the conclusion that the growing chains in the Suzuki reaction are being terminated by hydrolysis of the terminal boronate functionalities. Lower molecular weight species and starting materials with iodine groups present were removed by the extensive extractions performed, thus accounting for the low %I. Unfortunately, the Suzuki reaction for thiophene boronates is not applicable to polymerizations due to the ease of hydrolysis of the boronate. The Suzuki type reagents and techniques would be good candidates for synthesis of smaller 3 to 4 ring compounds as evidenced by the successful test reactions.

Polymer Quaternization

Cationic, water soluble polymers are easily formed from the neutral **PPT-NEt$_2$** by quaternization with bromoethane in THF as shown in Figure 3-10. The quaternized polymer, **PPT-NEt$_3$+**, was precipitated into acetone, collected, and dried at 50 ^{0}C under vacuum. Table 3-5 shows the elemental analysis results for **PPT-NEt$_3$+(96)[30]** and **PPT-NEt$_3$+(96-drop)[31]**, which are the quaternized forms of **PPT-NEt$_2$(96)[26]** and **PPT-NEt$_2$(96-drop)[28]**, respectively. The resulting polymers are soluble in acidic solution and pH = 7 water. The quaternization efficiency, as determined by ^{1}H NMR integration (comparison of the integral value of the terminal side chain protons,N-$CH_2CH_3^*$, to that of the O-CH_2^* protons [18:4 for 100% quaternization]), was on the order of 80-90% per sample. This is also reflected in the elemental analysis [26.24% Br by weight for complete alkylation compared to the 23.62% Br found for **PPT-NEt$_3$+(96-drop)[31]**.

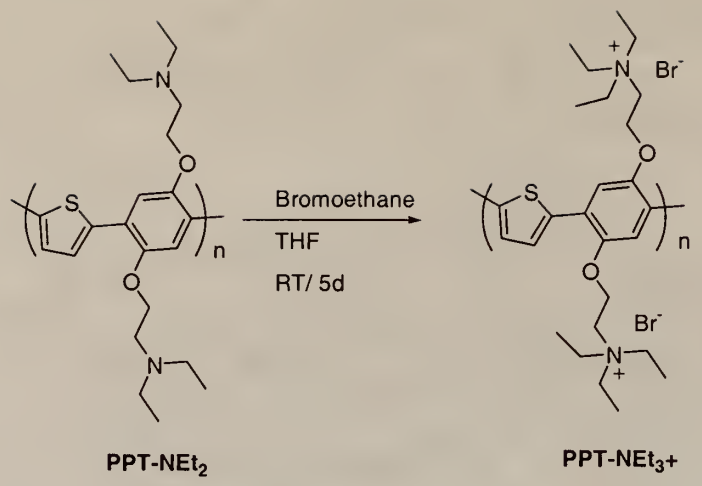


Figure 3-10. Quaternization of PPT-NEt_2 to form PPT-NEt_3+.

Physical Properties of PPT Type Polymers

Figure 3-11 shows the UV-Vis absorbance and photoluminescence spectra for **PPT-NEt_2[28]** in THF and **PPT-NEt_3+[31]** in H_2O (normalized for convenience). It is interesting to note the dramatic shift in absorbance maximum between the neutral and charged polymers. **PPT-NEt_2[28]** exhibits a λ_{max} at 460 nm with a corresponding molar absorptivity of about 18,000 L $mol^{-1}cm^{-1}$, while **PPT-NEt_3+[31]**'s λ_{max} is blue shifted 49 nm to 411 nm with a corresponding molar absorptivity of about 16,000 L $mol^{-1}cm^{-1}$. The blue shift of the π to π^* transition for these polymers may be due to a solvatochromic effect. Fine tuning of the λ_{max} could be achieved by controlling the extent of quaternization, as incomplete quaternization leads to a lower extent of hypsochromic shift.

Solution photoluminescence experiments revealed peak emission wavelengths of 519 nm and 494 nm for **PPT-NEt_2[28]** in THF and **PPT-NEt_3+[31]** in H_2O, respectively.

The excitation wavelength corresponded to the λ_{max} of each polymer's absorbance. The spectra display the typical characteristics of conjugated polymers in solution with a Stoke's shifted emission maximum and tailing broadly to higher wavelengths. Table 3-6 summarizes the optical properties for both the neutral and water soluble **PPT** polymers.

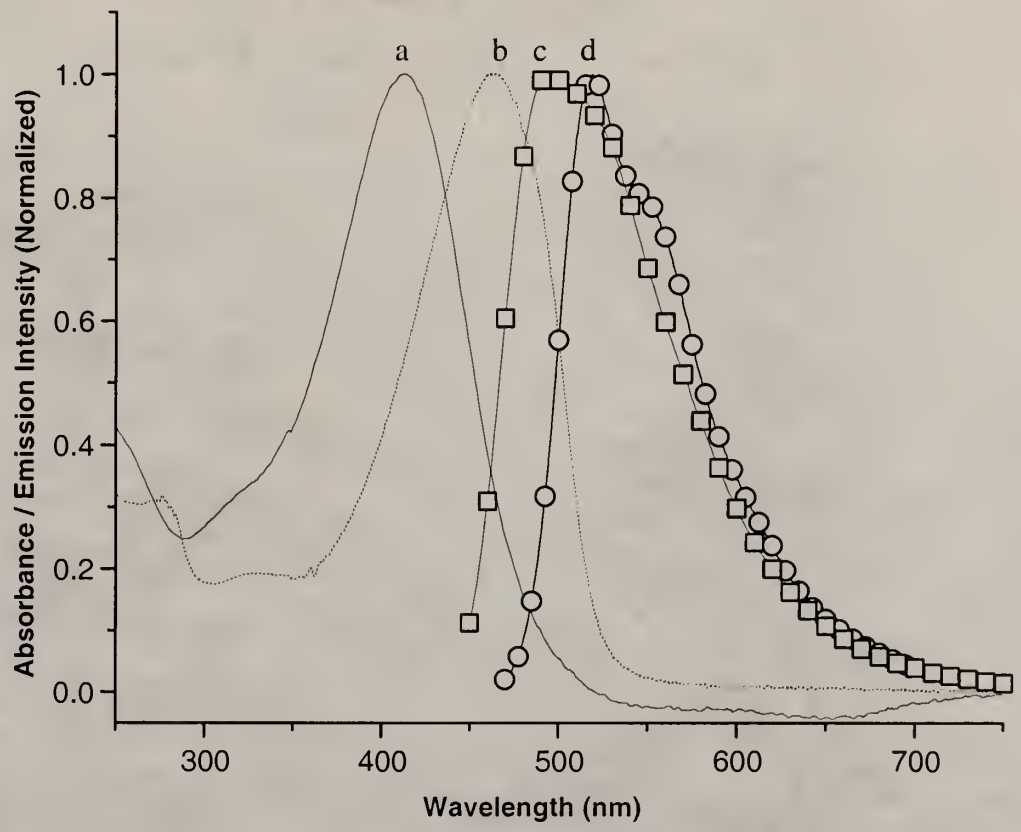


Figure 3-11. Normalized UV-Vis absorption and solution photoluminescence for PPT-NEt type polymers.

a) PPT-NEt_3+[**31**] UV-Vis absorption in H_2O.
b) PPT-NEt_2[**28**] UV-Vis absorption in THF.
c) PPT-NEt_3+[**31**] emission in H_2O.
d) PPT-NEt_2[**28**] emission in THF.

It is interesting to note that the trend of increased absorbance and emission intensity when moving from neutral to quaternized species for the **PPP-NEt_2** system was

not observed for the **PPT-NEt_2** polymers. In this case, quaternization led to a decrease in the emission output of the polymer in solution. Initial data from collaboration work have indicated that very little light is emitted from devices made from electrostatically deposited thin solid films of **PPT-NEt_3+[31]** excited by voltage application. Further work is needed to explain this occurrence, since NMR did not reveal any unexpected peaks for the polymer post quaternization.

Table 3-6. Summary of optical data for PPT-NEt type polymers.

Polymer	Absorbance λ_{max} (nm)	Film Color	Emission λ_{max} (nm)	Emission Color (Solution)
PPT-NEt_2[**28**]	460	Red	519	Green
PPT-NEt_3+[**31**]	411	Red	494	Green

Thermal de-alkylation of the amine sites can occur if the polymer is exposed to elevated temperatures, thus indicating a dynamic equilibrium at the amine sites. This de-alkylation is evidenced in the TGA for **PPT-NEt_3+[31]** shown in Figure 3-12 where an initial degradation event starting at 200 ^{0}C is observed, followed closely by loss of the triethylamine fragment. The initial weight loss event in the degradation of PPT-NEt_2[**28**] occurs at 250 ^{0}C corresponding to the loss of this same triethylamine type fragment. Both polymers have a final degradation occurring over 400 ^{0}C, attributed to the breakdown of the conjugated backbone and little residual mass remains.

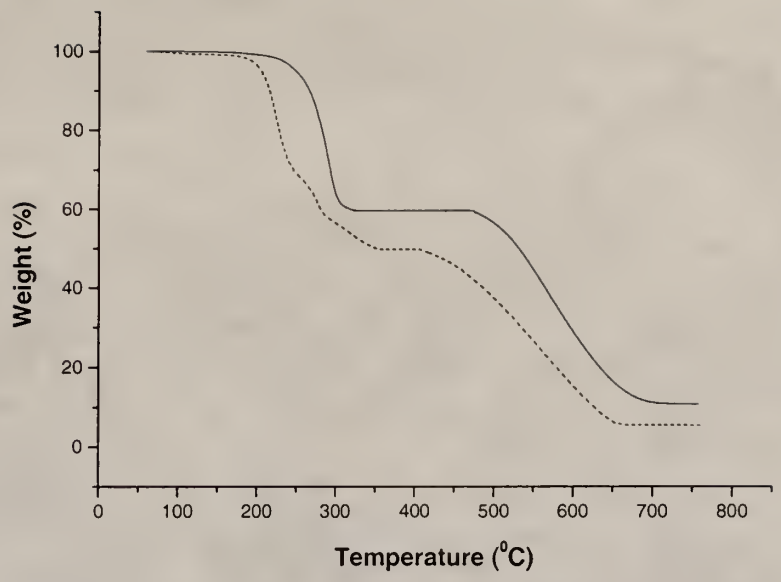


Figure 3-12. TGA thermograms for neutral and water soluble PPT-NEt under N_2.
a) —— PPT-NEt_2[**28**]
b) ----- PPT-NEt_3+[**31**]

Conclusions

A water soluble poly(*p*-phenylene-*co*-thiophene) (**PPT-NEt_3+[31]**) has been synthesized by a variety of modifications of Stille polymerization techniques. Maximum molecular weight was achieved in DMF using $PdCl_2(PPh_3)_2$ catalyst with slow addition of the 2,5-bis(trimethylstannyl)thiophene reagent. Again, as in the case of the **PPP-NEt_2** system, the polymer does begin to precipitate from the reaction over the coarse of the reaction, limiting the molecular weights. Polymerizations attempted in THF as solvent did not produce polymeric materials. Unfortunately, the use of **PPT-NEt_3+[31]** in electroluminescent devices appears unlikely due to low light emission in such devices. However, preliminary work has shown that the material may hold promise in electrostatically deposited thin layer systems for control over refractive index properties.

Adjustment of the number of **PPT-NEt_3+[31]** layers deposited and thickness of the layers dramatically changes and allows fine tuning of the refractive index of the transparent "window" created by the device.

Investigations of test reactions using Suzuki coupling techniques were successful using a 2,5 thiophene diboronate ester, however, the reagent was too susceptible to hydrolysis to allow the synthesis of high molecular weight polymers as evidenced by a lower absorption wavelength maximum than the Stille polymers. The 2,5 thiophene diboronate ester is a viable alternative to more hazardous and toxic 2,5-bis(trialkylstannyl)thiophene reagents for Pd coupling reactions to di-substitute thiophene in the 2,5 positions.

CHAPTER 4
CATIONIC POLY(*p*-PHENYLENE-ETHYNYLENE)'s

Introduction

Early Synthetic Attempts

Poly(*p*-phenyleneethynylene)'s [PPE's] are a class of polymers that are composed of alternating phenyl rings and triple bonds. They are structurally very similar to the much studied polymer, poly(*p*-phenylenevinylene) [PPV], in which electroluminescense from a conjugated polymer was first observed. PPE's did not receive the early attention of PPV, but research efforts have increased as the luminescent and conducting properties of PPE have been shown to be useful for explosive detection,[82] molecular wires that bridge nanogaps,[83] and polarizers for liquid crystalline displays.

The first synthesis of PPE oligomers was reported in 1983 and consisted of heating cuprous acetylide with diiodobenzene to a degree of polymerization of 10-12 (Figure 4-1a).[84] This type of approach, along with dehydrobromination of halogenated PPV's (Figure 4-1b),[85] and generation of PPE by electrochemical reduction of hexahalo-*p*-xylene (Figure 4-1c)[86], was unsuccessful in preparing well-defined systems without defects and solubility of the resulting species was low. PPE's have also been synthesized by ring-forming polycondensations, such as the reaction of acetylendicarboxylic amides with hydrazine sulfate in polyphosphoric acid (PPA) followed by thermal cyclization of the hydrazide groups (Figure 4-1d),[87] and modifications to synthesize a wide variety of rigid conjugated polyquinolines (Figure 4-1e).[88]

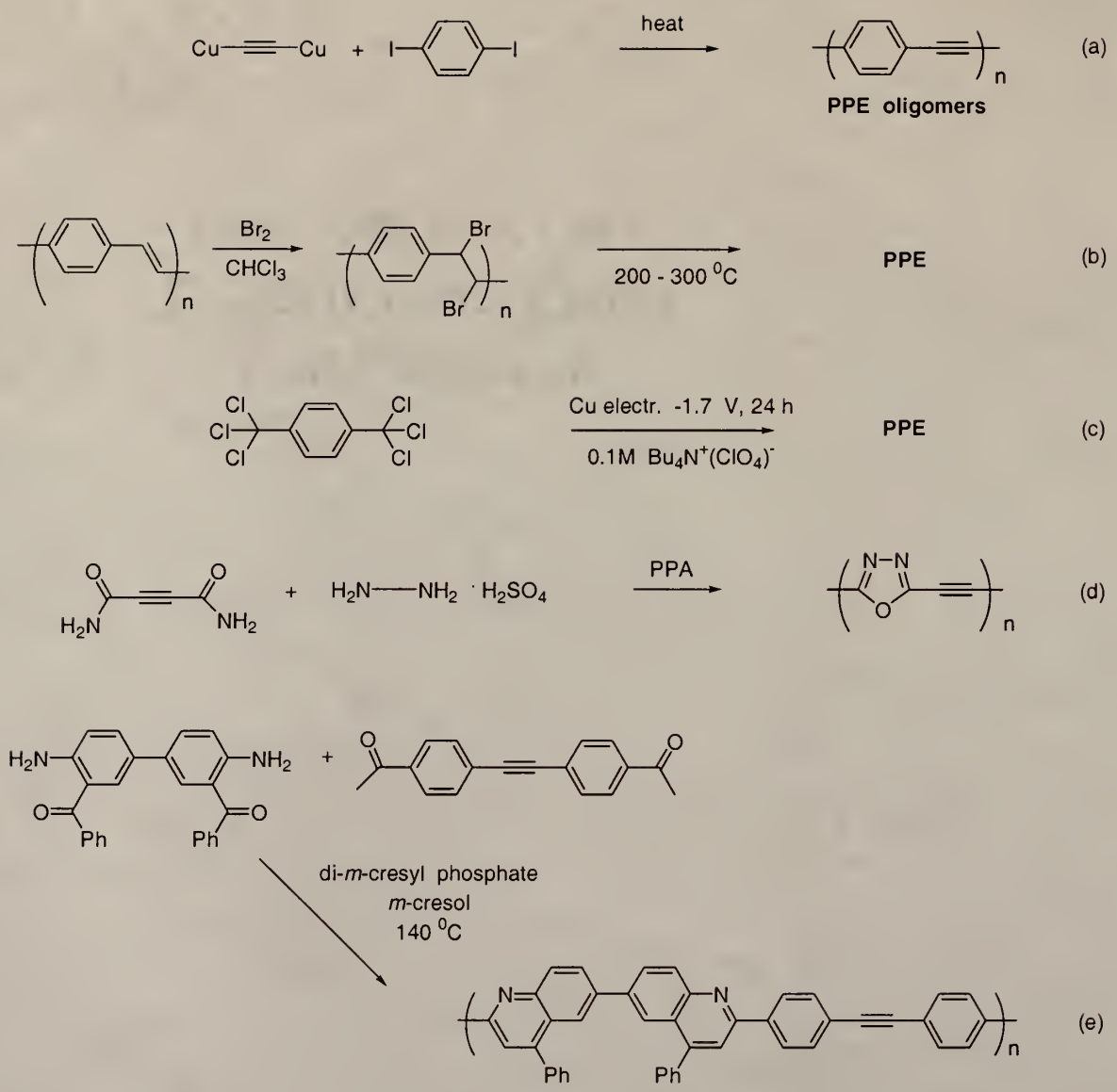
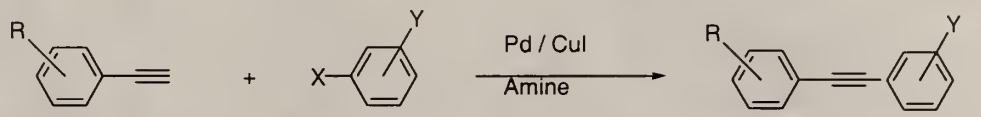


Figure 4-1. Early synthetic methodologies toward poly(*p*-phenyleneethynylene)'s [PPE].

Palladium (0) Coupling Reactions

Due to the limitations of the above routes, palladium cross coupling of terminal alkynes to aromatic bromides or iodides in amine solvents is often the preferred methodology to synthesize well-defined and soluble PPE's. This procedure is called the

Heck-Cassar-Sonogashira-Hagihara reaction and is one of the most frequently used carbon-carbon bond forming processes in organic chemistry.[89] Figure 4-2 outlines the simple mono-coupling reaction scheme. Obviously, for polymer synthesis both reagents are made difunctional and added to the reaction in precise stoichiometric amounts.



R = Alkyl, Aryl, OH, Ether, Ester

X = Br, I
Y = Ester, Nitrile, OR, NR_3, Alkyl

Figure 4-2. General reaction scheme for the Heck-Cassar-Sonogashira-Hagihara reaction.

Iodoaromatic compounds react faster and at lower temperatures than their corresponding bromoaromatic analogs. Electron withdrawing groups on the halo-aromatic compound increase the rate of the oxidative addition to the Pd(0). Elevated temperatures necessary for the bromo reagents can lead to cross-linking and defect formation. Choice of the amine solvent can have a dramatic effect on the reaction and it has been found that diisopropylamine is an excellent choice for use with iodoarenes. PPE polymerizations are conducted in concentrated solutions and amine solvents alone are not good solvents for PPE's, therefore THF, ethyl ether, and toluene are commonly used choices for co-solvents in the polymerizations.

The air stable, commercially available Pd(II) catalyst, $PdCl_2(PPh_3)_2$, is often used as the source of Pd(0) in the coupling reaction and must be reduced to the active Pd(0)

species as outlined in Figure 4-3. Two molecules of a cuprated alkyne transmetallate the Pd catalyst precursor and a symmetrical butadiyne is reductively eliminated, leaving an active Pd(0) catalyst. $PdCl_2(PPh_3)_2$ is used in 0.1-5 mol % amounts and varying amounts of CuI are used as an alkynyl activator.[90] Activation of the Pd(II) catalyst requires consumption of the alkyne reagent which must be adjusted accordingly in polymerizations to ensure a 1:1 stoichiometric balance with the haloaromatic compound. A possible approach to solving the stoichiometric balance problem is the "pre-activation" of the catalyst by addition of a monofunctional alkyne (such as phenylacetylene) to the Pd(II) catalyst, thereby converting it to Pd(0). The catalyst solution could then be added to the polymerization reagents and the diyne by-product of the catalyst activation would not interfere with the stoichiometric balance.

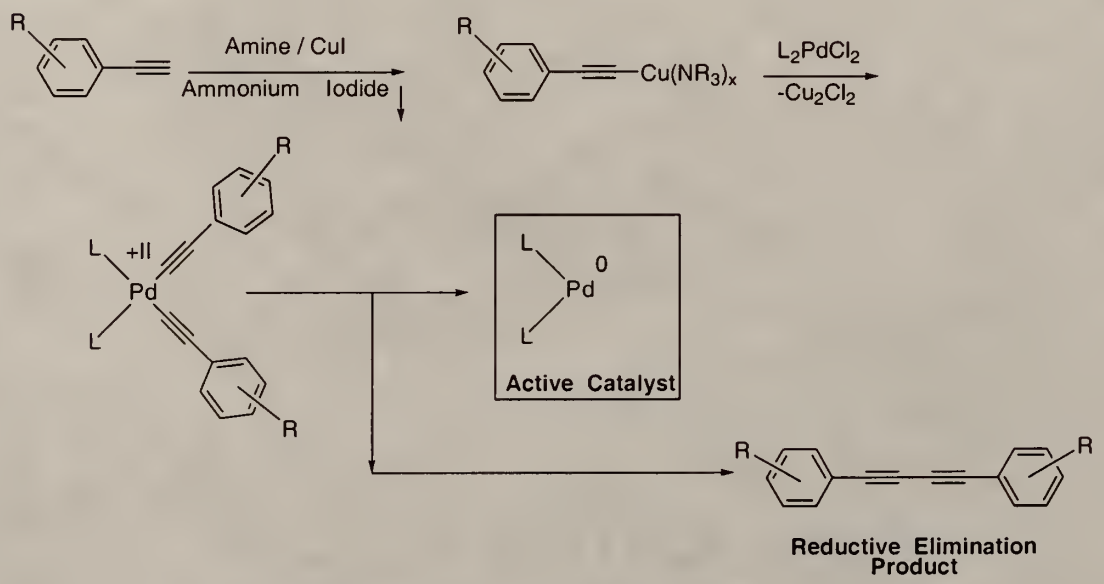


Figure 4-3. Activation of Pd(II) compound to active Pd(0) catalyst.

Dialkoxy-Poly(*p*-phenyleneethynylene)'s

The first soluble PPE derivatives were synthesized by Giesa with the incorporation of long alkoxy groups to the rigid PPE backbone.[91] Degrees of polymerization on the order of 10-15 were achieved as a deeply colored solid was recovered. Solubility was low and the deep coloration indicated extreme interchain packing or some degree of crosslinking. Crosslinking can occur between internal or terminal triple bonds in the polymer chain, lowering solubility and darkening the color of the material and subsequently promoting inter-chain packing. An improved synthesis (see Scheme 4-4) of similar PPE's was achieved by Moroni et al. with degrees of polymerization of approximately 20.[92] These workers did not take into account the activation of the palladium catalyst, thus lowering molecular weights and introducing diyne defects in the backbone.

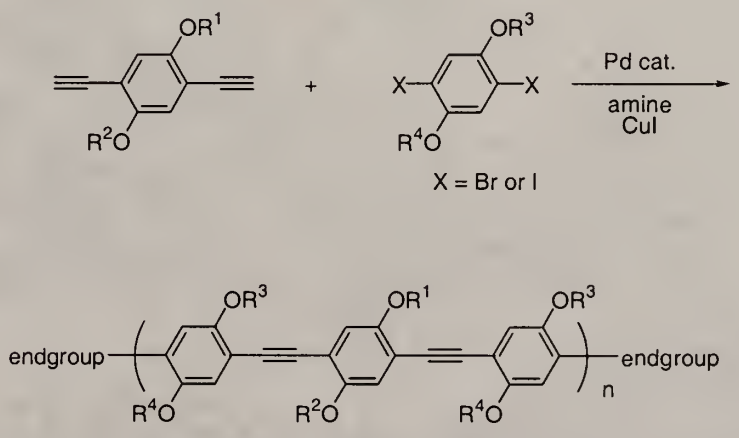


Figure 4-4. Synthesis of dialkoxy poly(*p*-phenyleneethynylene)'s via the Sonogashira reaction.

Reduction of reaction temperatures to lower than 70 ^{0}C by Wrighton et al. in the coupling of 2,5-diiodo-1,4-dialkoxybenzenes to 2,5-diethynyl-1,4-dialkoxybenzenes in a

diisopropylamine/toluene mixture under $PdCl_2(PPh_3)_2$/CuI catalysis led to polymers without crosslinking and degrees of polymerization of up to 100.[93] The same group prepared interesting dialkoxy-substituted copolymers with 3-(dimethylamino)propyl and 7-carboxy-heptyl groups.[94] Weder et al.[95] utilized the branched solubilizing ethylhexyloxy and linear octyloxy groups to prepare a polymer with a reported degree of polymerization of 230, which were summarily reflected in the similar work of Swager and coworkers who limited the molecular weight by the use of an imbalanced reaction stoichiometry to ensure defined iodine endgroups.[96]

Other classes of PPE's have been created via the Sonogashira reaction that mix di-alkoxy-substituted diiodides with different aromatic diynes. Examples include West's use of 1,4-diethynylbenzene[97] (Figure 4-5a) and Swager's use of a1,4-diethynylpentiptycene monomer to provide bulky chain spacing side-groups[98] (Figure 4-5b) or a bisamide compound better film forming properties (Figure 4-5c).[99] Aryl- and alkyl-substituted PPE's, which resemble a "true" unsubstituted PPE the most, were first reported in 1995 by Bunz and Müllen (Figure 4-5d).[100] A complete coverage of all PPE type polymers synthesized by Pd(0) coupling methodologies would be impossible in this dissertation, however, two excellent reviews by Giesa and Bunz on the subject matter are available for reference.[101] Extensive work has also been accomplished in the field of metal to ligand charge transfer between PPE's and coordinated metallic species.[102]

The utility of the Sonogashira reaction for synthesizing well-defined PPE's, along with its tolerance for functional groups, makes it applicable for incorporation of 2,5-dialkoxyamine-phenylene units into a PPE backbone structure. These units can be protonated with acidic treatment or quaternized with ethylbromide to provide an

interesting new class of polyelectrolyte. In general, such polymers should be yellow in color and emit in the green region of the visible color spectrum. Due to the extensive rigid-rod character of PPE's, special care will have to be taken with the resulting materials to determine the effect different side chains on the second phenylene ring in the repeat unit will have on the solubility of the initial neutral polymer and subsequently the effect of bulky organic groups on the properties of the post-polymerization quaternized polymer. If successful, this set of PPE polymers may provide polymers that emit in a similar wavelength range as the poly(*p*-phenylene-*co*-thiophenes) [PPT's] discussed in Chapter 3 and are more efficient emitters, which are capable of being cast as free standing thin films.

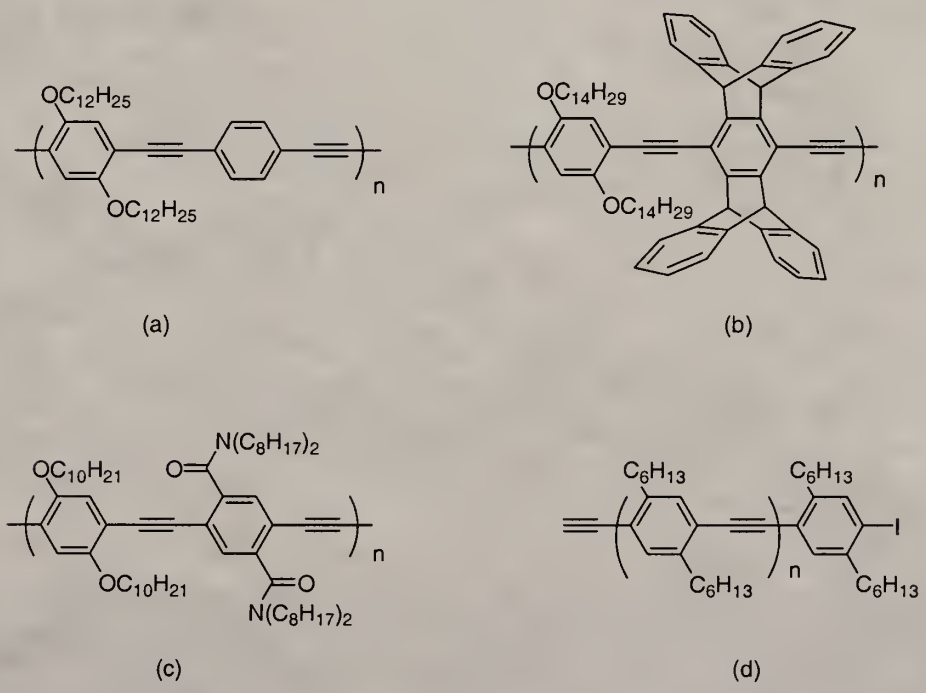
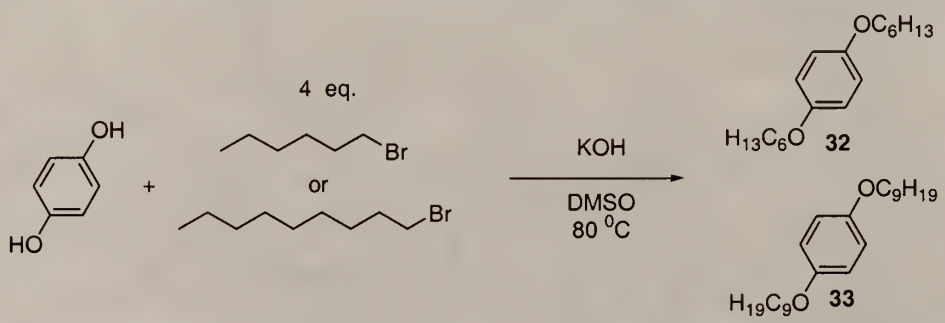


Figure 4-5. Representative structures of synthetic modifications to poly(*p*-phenyleneethynylene)'s.

Results and Discussion

Monomer Syntheses

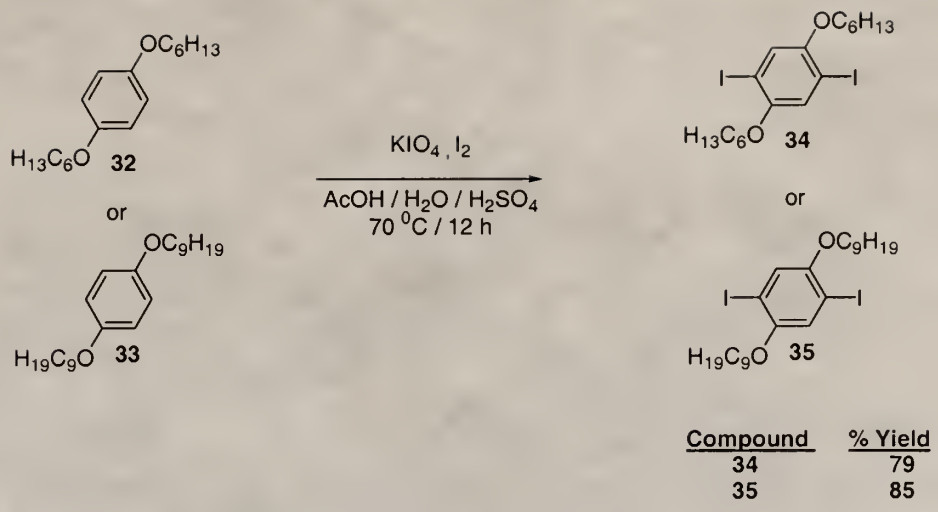
As illustrated in Figure 4-4, Sonogashira couplings require the usage of a di-haloaromatic and a di-ethynylaromatic for an AA-BB type polymerization. Initial monomer synthesis focused on the di-ethynyl reagent; the substitution of which will greatly affect the solubility characteristics of the resulting polymer. Figure 4-6 outlines the Williamson etherification procedure used to alkylate hydroquinone with primary alkyl bromides.[103] A suspension of powdered KOH was stirred in dry DMSO for one hour followed by addition of hydroquinone and either hexyl- or nonyl-bromide. The reactions were heated to 80 ^{0}C for 12 hours, cooled, poured into ice water, and extracted with hexanes. The organic layer was subsequently washed with 1M NaOH, water, brine,



Compound	% Yield
32	83
33	79

Figure 4-6. Williamson etherification to synthesize various 1,4-dialkoxyphenylene's.

and dried over $MgSO_4$. Removal of the solvent via reduced pressure evaporation led to the isolation of reddish solids. The solids, 1,4-bis(hexyloxy)benzene (**32**) and 1,4-bis(nonyloxy)benzene (**33**), were purified by recrystallization from ethanol giving white solids in 83 and 79 percent yields, respectively.

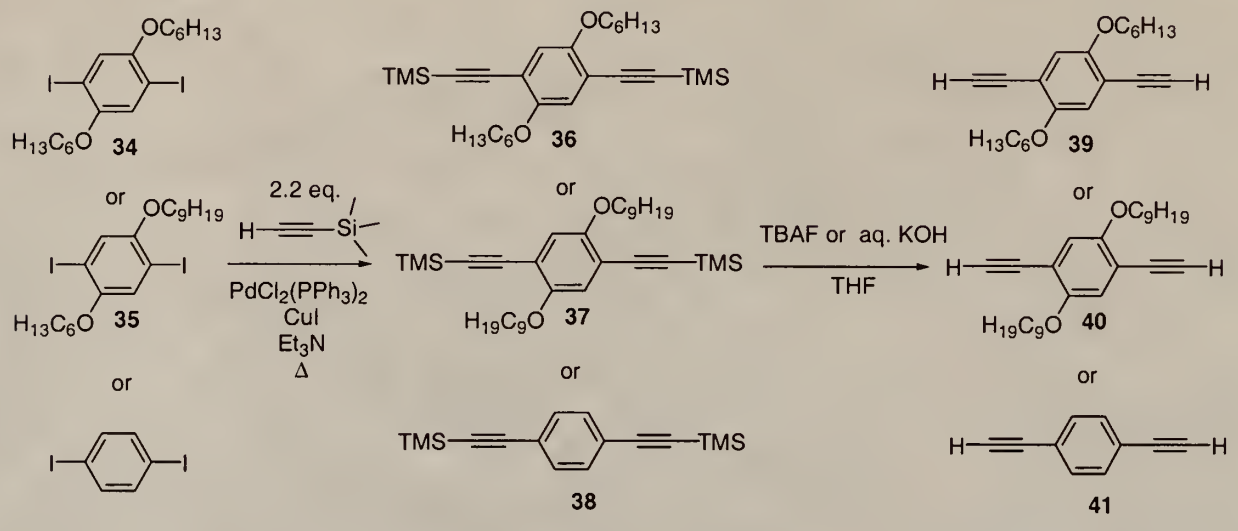


Compound	% Yield
34	79
35	85

Figure 4-7. Iodination of various 1,4-dialkoxybenzene's.

The 1,4-bis(alkoxy)benzenes (**32** and **33**) were iodinated under acidic conditions using potassium periodate, iodine, and a mixed solvent system consisting of 90:7:3 HOAc/ H_2O/ H_2SO_4 by volume with heating to yield 1,4-dialkoxy-2,5-diiodobenzenes (**34** and **35**) as shown in Figure 4-7 in 79 and 85 percent yields as white crystals. The di-iodides, **34** and **35**, along with 1,4-diidobenzene were then subjected to a Sonogashira coupling with (trimethylsilyl)acetylene in the presence of $PdCl_2(PPh_3)_2$ and CuI catalysts in an amine solvent. The 1,4-bis((trimethylsilyl)ethynyl) compounds[**36-38**] were isolated via filtration of the reaction to remove amine salts and passed through a filter plug of silica gel using toluene as eluent. After removal of the solvent, crude red solids were obtained and recrystallized twice from ethanol to yield white crystals. The 1,4-bis((trimethylsilyl)ethynyl) compounds were treated with either tetrabutylammonium fluoride or aqueous KOH in THF to remove the TMS groups. The diethynyl compounds (**39-41**) shown in Figure 4-8 were recovered in overall 70 to 82 percent yields based on

the appropriate starting di-iodide compound as light yellow or white crystals. Elemental analysis results for compounds **39-41** are listed in Table 4-1.



Compound	% Yield
39	75
40	70
41	82

Figure 4-8. Synthesis of various 1,4-diethynylphenylene monomers.

The previously described di-iodide compound 2,5-bis(3-[*N,N*-diethylamino]-1-oxapropyl)-1,4-diiodobenzene **(DINEt)** was used in conjunction with the above di-ethynyl compounds for Sonogashira polymerizations to provide a functional amine site to be quaternized after polymerization (see Chapter 1). Synthesis of 2,5-bis(3-[*N,N*-diethylamino]-1-oxapropyl)-1,4-diethynylbenzene, produced by Pd(0) coupling of **DINEt** with trimethylsilylacetylene and treatment with base, was attempted in order to have a companion reagent to **DINEt**, which upon Sonogashira polymerization with **DINEt** would produce a PPE with every phenylene ring possessing alkoxyamine side chains.

Purification of the 2,5-bis(3-[*N*,*N*-diethylamino]-1-oxapropyl)-1,4-diethynylbenzene to a level satisfactory for use in step growth polymerizations was hindered greatly by the

Table 4-1. Elemental analysis results for PPE monomers and polymers.

Species		%C	%H	%N	%I or Br	Anal. Calcd. for
Compound 39	Theo.	80.93	9.27	-	-	$C_{22}H_{30}O_2$
	Exp.	81.20	9.15	-	-	
Compound 40	Theo.	81.89	10.32	-	-	$C_{28}H_{42}O_2$
	Exp.	82.02	10.68	-	-	
Compound 41	Theo.	95.20	4.80	-	-	$C_{10}H_6$
	Exp.	95.60	4.60	-	-	
PPE-NEt_2/H [51]	Theo	71.78	7.26	5.98	1.05	$C_{28}H_{34}N_2O_2I_{0.04}$
	Exp.	70.25	7.08	5.35	1.05	
PPE-NEt_2/ OC6 [52]	Theo.	75.64	9.20	4.41	0.67	$C_{40}H_{58}N_2O_4I_{0.10}$
	Exp.	72.10	7.89	4.01	0.67	
PPE-NEt_2/ OC9(High) [53]	Theo.	76.84	9.81	3.90	0.55 (I)	$C_{46}H_{70}N_2O_4I_{0.03}$
	Exp.	76.11	9.79	3.47	0.55 (I)	
PPE-NEt_2/ OC9(20) [54]	Theo.	76.98	9.83	3.90	0.37 (I)	$C_{46}H_{70}N_2O_4I_{0.02}$
	Exp.	75.66	9.64	3.41	0.37 (I)	
PPE-NEt_3+/ OC9(20) [56]	Theo.	64.37	8.64	3.00	17.13 (Br)	$C_{46}H_{70}N_2O_4$ ·2 C_2H_5Br
	Exp.	66.06	8.92	3.03	12.58 (Br)	$C_{46}H_{70}N_2O_4$ ·1.35 C_2H_5Br

extremely polar amine sites, which prevented column chromatography. Other means of purification were unsuccessful in that distillation under reduced pressure resulted in the

cleavage of the triethylamine side groups and attempted recrystallization led to both impurities and the desired compound to crystallized from the chosen solvents.

Taking into account the limitations imposed to purification by the polar amine side groups of **DINEt**, it was desirous to have an alternate di-iodo monomer that possesses the ability to form cationic amine sites, but does not contain amine sites from the initial compound synthesis . A route found in the literature used bromo-terminated alkyl groups as side chains on benzene that were treated with triethylamine, imparting water solubility with the resulting quaternized amine functionalities.[104] Figure 4-9 outlines the synthesis of 2,5-bis(6-bromohexyl)-1,4-diiodobenzene which provides an optional monomer to **DINEt**. It should be noted that this monomer does not have alkoxy, but rather alkyl side chains and upon incorporation into a polymer backbone would raise the energy of the π to π^* transition compared to alkoxy containing PPE's.

Isolation of intermediate **43** was a challenging step in that that the presence of unreacted starting material **42,** which will prevent isolation of compound **44** in later steps, must be removed by careful spinning band distillation under reduced pressure. The distillation technique and equipment are dependent on user ability and several trials had to be performed in order to maximize the separation ability of the apparatus. A rather large spinning band column was used as 100g batches of compound **43** were typically synthesized. Figure 4-10 shows the GC chromatogram of the reduced pressure distillation of compound **43** using a simple vigreux column followed by a purification using the spinning band technique. The initial simple distillation is not necessary for purification, but was conducted to show the separation advantages of the spinning band column. The small amount of 1,6-dimethoxyhexane present in the post- spinning band

distillation GC will not affect the next reaction and its presence is due to the fact that only one major fraction was collected with priority on avoiding the higher boiling starting material **42**. Additional glassware pieces for the distillation apparatus have been designed and allow for the collection of multiple fractions without disturbing the reduced pressure of the column. Small changes in the pressure of the distillation during operation will negate the separation benefits of the technique.

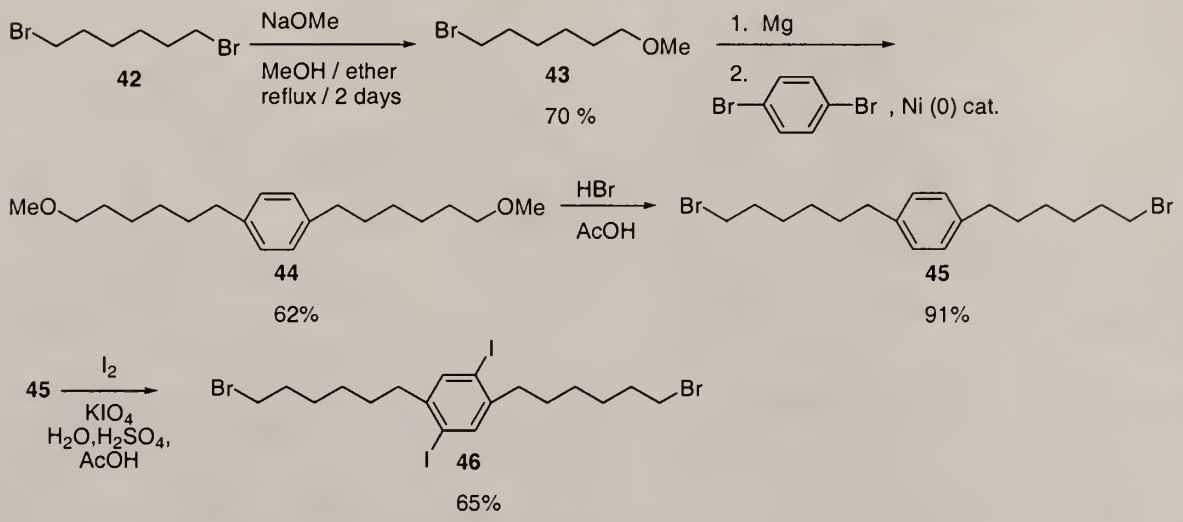


Figure 4-9. Synthesis of 2,5-bis(6-bromohexyl)-1,4-diiodobenzene.

Pure compound **43** was reacted with Mg metal to form the Grignard reagent and is added to a solution of 1,4-dibromobenzene and nickel catalyst to form compound **44**, which was isolated by simple vacuum distillation. The methoxy endroups were converted to bromine by refluxing in a hydrogen bromide/acetic acid solution and isolated as a colorless solid after recrystallization. This step was necessary as the iodination conditions used to synthesize compound **46** were shown to cleave the methoxy groups, giving a complex mixture of inseparable products. Compound **46** was collected

in 65% yield as a white crystalline solid after recrystallization from methanol, based on the amount of compound **45** used (overall 26 % yield based on starting compound **42**).

Rehahn et al. demonstrated the technique of "protecting" the bromine groups by etherification with phenol and reacting their 2,5-bis(6-phenyoxyhexyl)-1,4-dibromobenzene with various phenylene boronic reagents to create poly(*p*-phenylene)'s. The phenoxy end groups could be converted post-polymerization into iodo functionalities by treatment with trimethyliodosilane followed by exposure to triethylamine to produce charged, cationic amine sites along the backbone of the polymer (see Figure 4-11). These PPP type polymers possessed significant solubility in water, but it should be noted that more rigid PPE polyelectrolytes should inherently have more complex and lower solubility behaviors in water.

The same methodology could be used to synthesize PPE type polymers with 6-phenoxyhexyl sides that could undergo the above transformation to cationic amine sites. The Williamson etherification of compound **46** with phenol is outlined in Figure 4-12. Compound **50** could be used in Sonogashira type polymerizations to create interesting PPE's, see Figure 4-13, which can be treated in the same manner as the PPP's in Figure 4-11 to achieve charged amine sites along the backbone. As the purpose of this body of work is to focus on dialkoxy substituted PPE's, polymerizations utilizing 2,5-bis(6-phenoxyhexyl)-1,4-diiodobenzene [**50**] were not conducted. However, the somewhat difficult monomer synthesis has been fine tuned to allow the pursuit of these type of PPE polymers by future workers.

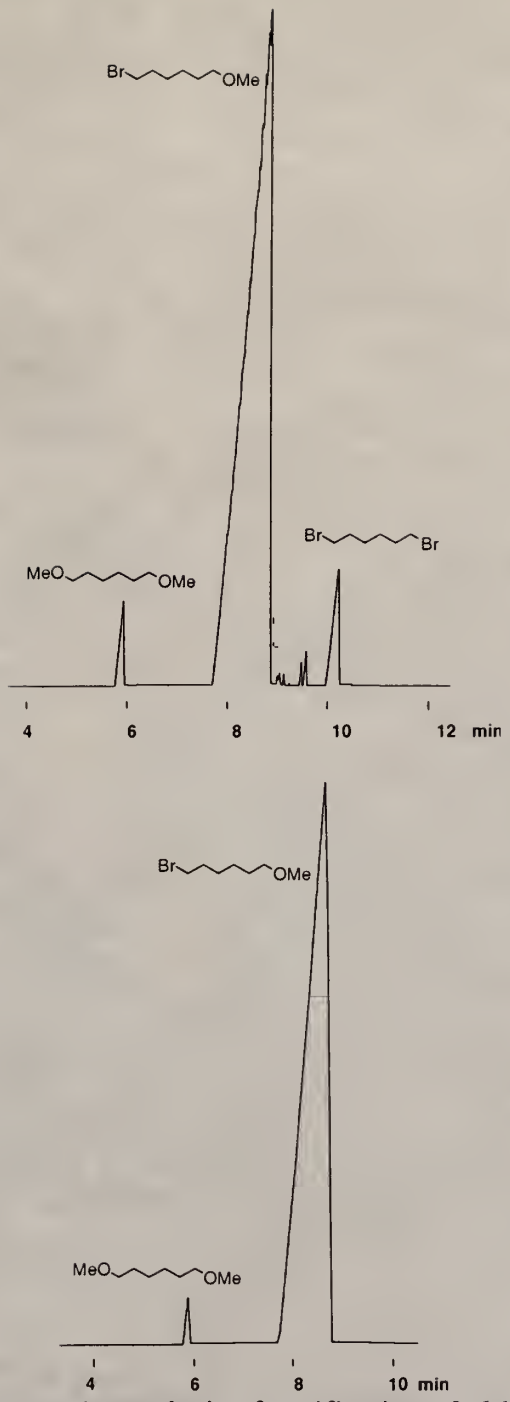


Figure 4-10. Gas chromatography analysis of purification of 6-bromohexylmethylether (**43**) by vacuum distillation using (a) simple vigreux column and (b) spinning band column.

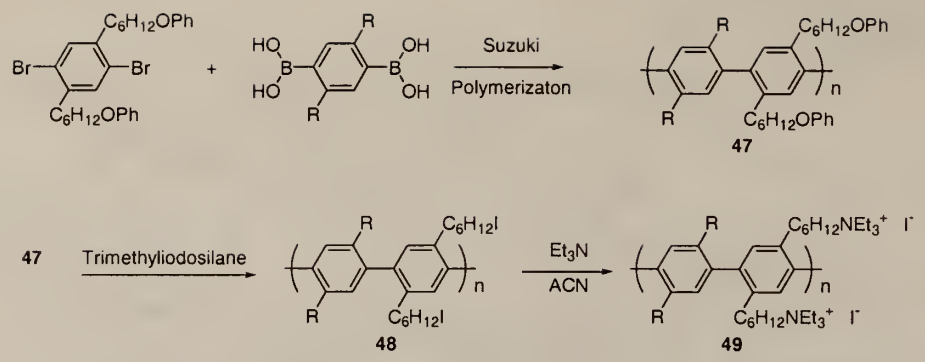


Figure 4-11. Rehahn's route to cationic PPP's.

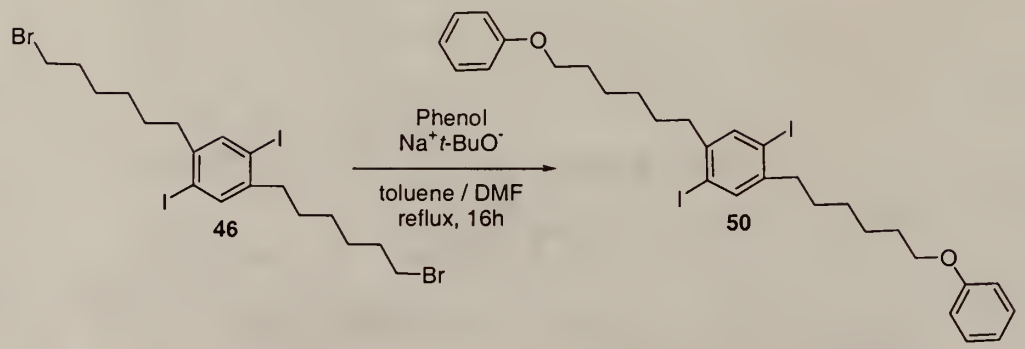


Figure 4-12. Williamson etherification to "protect" bromo endgroups.

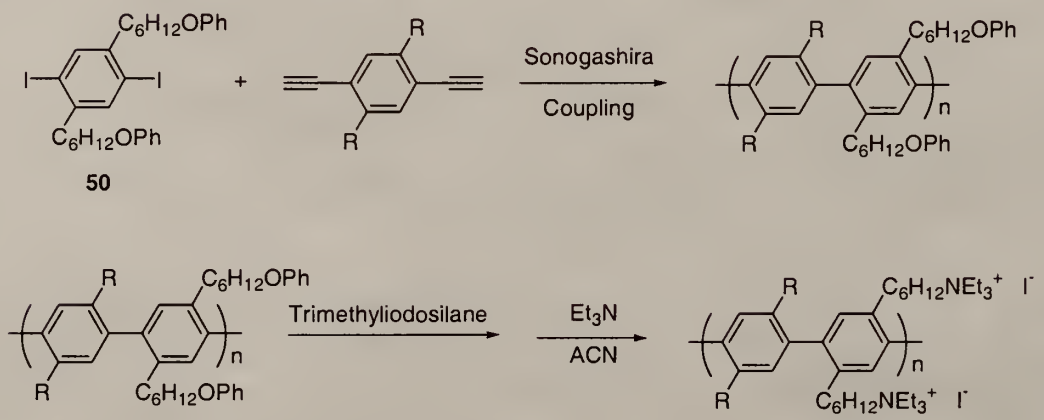


Figure 4-13. Envisioned application of Rehahn's strategy to PPE's.

Neutral Polymer Syntheses

The general Sonagashira polymerization is outlined in Figure 4-14. **DINEt**, di-ethynyl compound, CuI co-catalyst, and Pd catalyst of choice, were stirred in a solution of toluene and amine (triethylamine or diisopropylamine) with heating to 70 ^{0}C. Temperatures above 70 ^{0}C are known to promote crosslinking in the PPE chains, along with undesired diyne defects, and were therefore avoided. When Pd(II) catalysts are employed, the amount of di-ethynyl compound should be adjusted to account for reduction of the catalyst to Pd(0), as shown in Figure 4-3. Pd(0) catalysts, such as $Pd(PPh_3)_4$, are effective for the coupling and do not need to be reduced before beginning the catalytic cycle, but careful exclusion of O_2 from the reaction must be conducted. For the polymerizations in this study, diisopropylamine and $Pd(PPh_3)_4$ were used in all couplings.

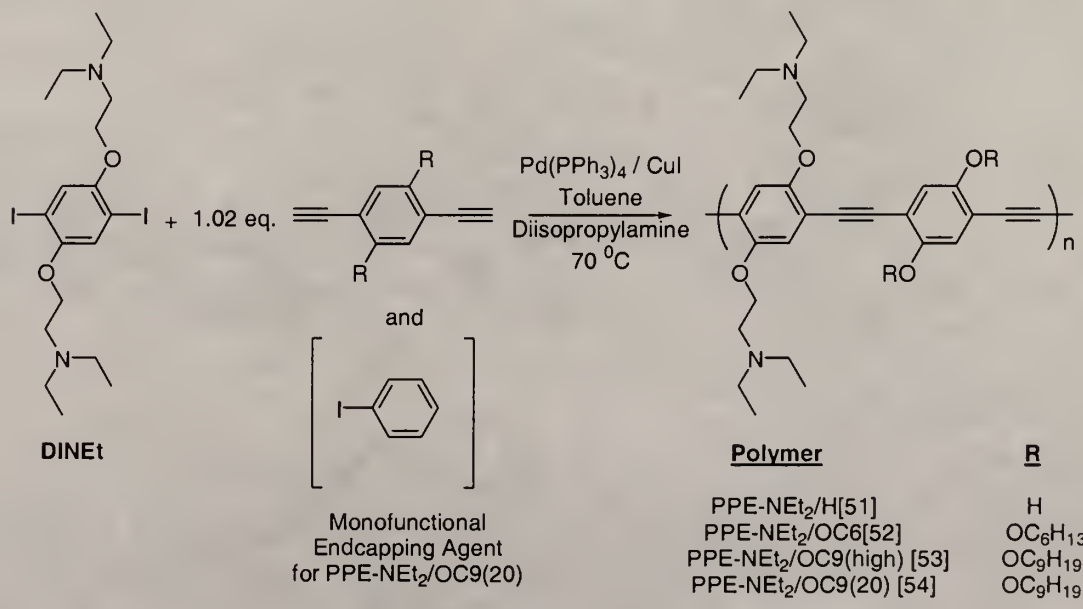


Figure 4-14. General synthesis for alkoxy-amine containing PPE's.

Initial synthetic attempts at producing useful PPE's were performed with the coupling of **DINEt** to 1,4-diethynylbenzene using toluene / diisopropylamine solvent system (0.05M in **DINEt**) and 5 mol% $Pd(PPh_3)_4$ / CuI catalysts (**PPE-NEt$_2$/H[51]**). A slight excess of di-ethynyl compound is used (~1 mol %), even with an initial Pd(0) catalyst, to account for unavoidable side reactions of the compound. After a reaction time of 24 hours, a noticeable amount of material was precipitating from the reaction flask. After cooling the reaction after 48 hours, the mixture was poured into cold ethanol and a yellow solid recovered in nearly quantitative yield. This yellow material was insoluble in hot chloroform, THF, or toluene. This result was not unexpected as PPE's are known for their high susceptibility to packing when isolated as solids and subsequent poor solubility. **PPE-NEt$_2$/H[51]** was extracted with hot ethanol overnight, in an attempt to remove catalyst residues. The polymer did appear to swell with solvent and was dried overnight under vacuum. Elemental analysis was performed on the polymer sample to help determine if crosslinking had occurred during polymerization. Carbon, hydrogen, and nitrogen values are close to the predicted values for the polymer repeat unit structure. Determination of molecular weight (via ^{1}H NMR or GPC) was excluded by the insolubility of the material. Elemental analysis of the material was consistent with the proposed repeat unit structure (see Table 4-1).

Longer alkoxy groups were then used on the di-ethynyl reagent in hopes of adding solubility in organic solvents to the neutral PPE's. Polymerization of compound **39**, 1,4-diethynyl-2,5-bis(hexyloxy)benzene, with **DINEt** under the same conditions as listed above for **PPE-NEt$_2$/H[51]** was undertaken (**PPE-NEt$_2$/OC6[52]**). Over the coarse of 24 hours, the growing polymer remained in solution with no evidence of a

polymer coating on the reaction vessel. When excited by a UV lamp, an intense yellow-green emission was observed. Upon cooling, excess solvent was removed and the remaining solution was precipitated into MeOH. Quantitative yield of a yellow-orange material was recovered and extracted successively with MeOH, acetone, and $CHCl_3$ via Soxhlet extraction. Only 2% of the initially precipitated material dissolved after stirring in boiling chloroform, toluene, or 1,2-dichlorobenzene. The fact that the polymer was soluble during the polymerization and insoluble after precipitation, supports the hypothesis that the hexyloxy chains are sufficiently long to make the polymer soluble in toluene, but aggregation and packing ability are at such high levels for the solid, precipitated **PPE-NEt$_2$/OC6[52]** that the polymer chains can no longer be separated and solvated by common organic solvents. Elemental analyses of the insoluble materials is shown in Table 4-1.

In order to overcome the solubility problem, the longer nonyl-oxy side chain reagent **40** was used in the Sonogashira polymerization. Two polymerizations were performed using the same conditions as the above PPE polymers. One reaction was conducted to produce the highest molecular weight polymer possible (**PPE-NEt$_2$/OC9(High)[53]**) and the other polymerization was conducted with the addition of a small amount of iodobenzene to limit chain length (theoretically calculated to give a degree of polymerization of 20 (40 rings) using simple step-growth polymerization equations) to synthesize **PPE-NEt$_2$/OC9(20)[54]**. The addition of the endcapping reagent should limit chain length to improve solubility and give definitive ^{1}H NMR signals for determination of number average molecular weights. During the coarse of polymerization, **PPE-NEt$_2$/OC9(High)[53]** formed a gel-like suspension, indicating a

very high extent of polymerization, while **PPE-NEt$_2$/OC9(20)[54]** remained soluble. The "gel" was fully dissolved by the addition of an excess of chloroform. Both reactions were precipitated into acetone after 24 hours and the collected polymers were washed thoroughly with hot ethanol, acetone, and acetonitrile.

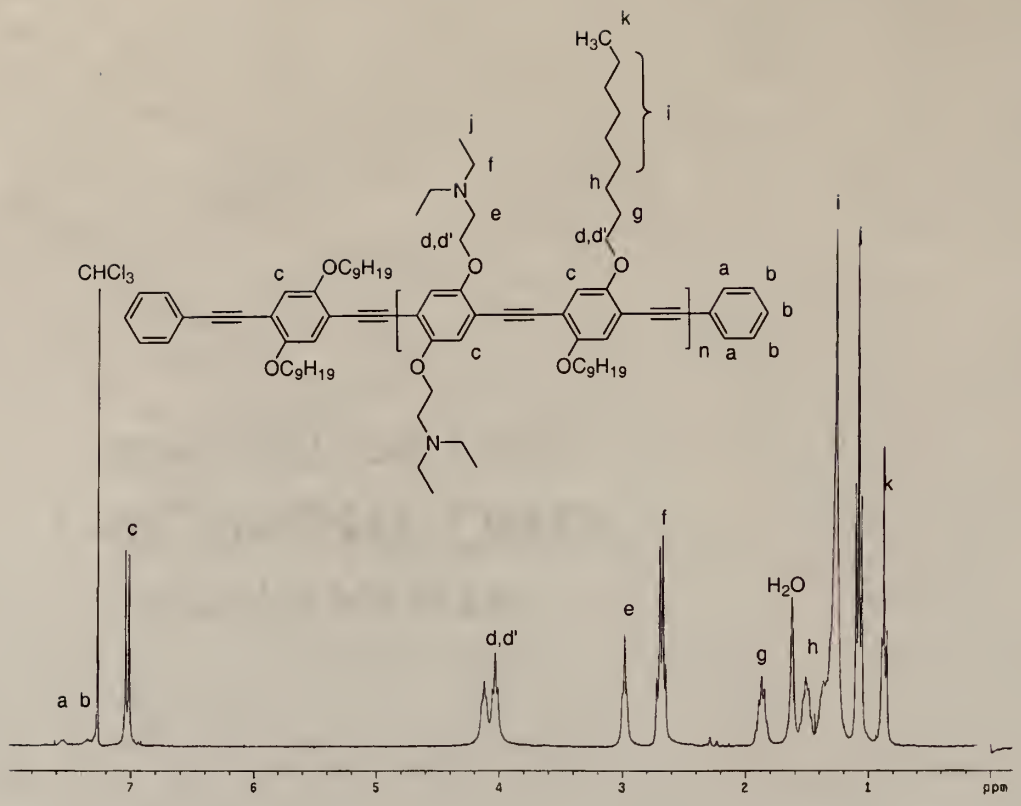
PPE-NEt$_2$/OC9(High)[53] became insoluble upon complete drying with light heating under vacuum. Elemental analysis of **PPE-NEt$_2$/OC9(High)** indicated 0.55% iodine by weight present in the sample which with the assumption that there is one iodine molecule per chain indicates a degree of polymerization of 34 (68 rings). A small amount of the dried **PPE-NEt$_2$/OC9(20)[54]** would dissolve in refluxing chloroform and a crude ^{1}H NMR was acquired for the soluble portion. The spectrum was consistent with the proposed polymer structure, but endgroup analysis was not definitive due to the low concentration of the NMR sample and the inherent fractionation of the material.

The ability of the chains to pack in well-dried solid form prevents re-solvation of the polymer chains and renders the materials unusable. After the initial work on the polymers above, it was decided to repeat the **PPE-NEt$_2$/OC9(20)[54]** polymerization and prevent the complete drying of the material. Work with **PPE-NEt$_2$/OC9(20)[54]** was chosen over **PPE-NEt$_2$/OC9(High)[53]** to ensure the greatest chance of maintaining solubility. With a degree of polymerization of 20, **PPE-NEt$_2$/OC9(20)[54]** will have attained its maximum optical absorption and emission and if solubility can be maintained will provide a useful polymer. It was decided not to extend the length of the alkoxy chain to help prevent chain packing, as such an increase in the organic nature of the polymer would be detrimental to the desired water solubility of the cationic derivatives to be produced after polymerization. The second synthesis of **PPE-NEt$_2$/OC9(20)[54]**

provided a polymer that maintained solubility to a reasonable level in chloroform (~10 mg/mL) after drying overnight in a steady stream of air. The polymer was bright yellow in color indicating little crosslinking or diyne defects had occurred and was recovered in high yield (98%).

Determination of the molecular weight of the rigid **PPE-NEt$_2$/OC9(20)[54]** via standard gel permeation chromatography (GPC) proved inconclusive. Although sufficiently soluble in chloroform to perform the analysis, peaks detected by UV absorption appeared only at the end of the column volume. The PPE polymer interacted with and adsorbed to the column packing material in such a way as to prevent separation by size. This is not an uncommon phenomenon, especially with polar polymers which can possibly bind to the column material. The rigid nature of the polymers, excluding column "sticking" effects, normally cause a decrease in the retention time of the sample when compared to polystyrene standards of the approximate same molecular weight further complicating molecular weight determination by this method.

^{1}H NMR, UV absorbance, and film casting were used to substantiate that the material was polymeric. Free standing orange films of **PPE-NEt$_2$/OC9(20)[54]** could be cast from chloroform solutions onto glass or Teflon® substrates. Figure 4-15 shows both the ^{1}H and ^{13}C NMR for **PPE-NEt$_2$/OC9(20)[54]** in $CDCl_3$ which gave expected shift values with the proton peaks appearing as broad multiplets with poor splitting. Figure 4-16 shows an expansion of the aromatic region, along with integral values for the peaks in order to calculate an approximate degree of polymerization for **PPE-NEt$_2$/OC9(20)[54]**.



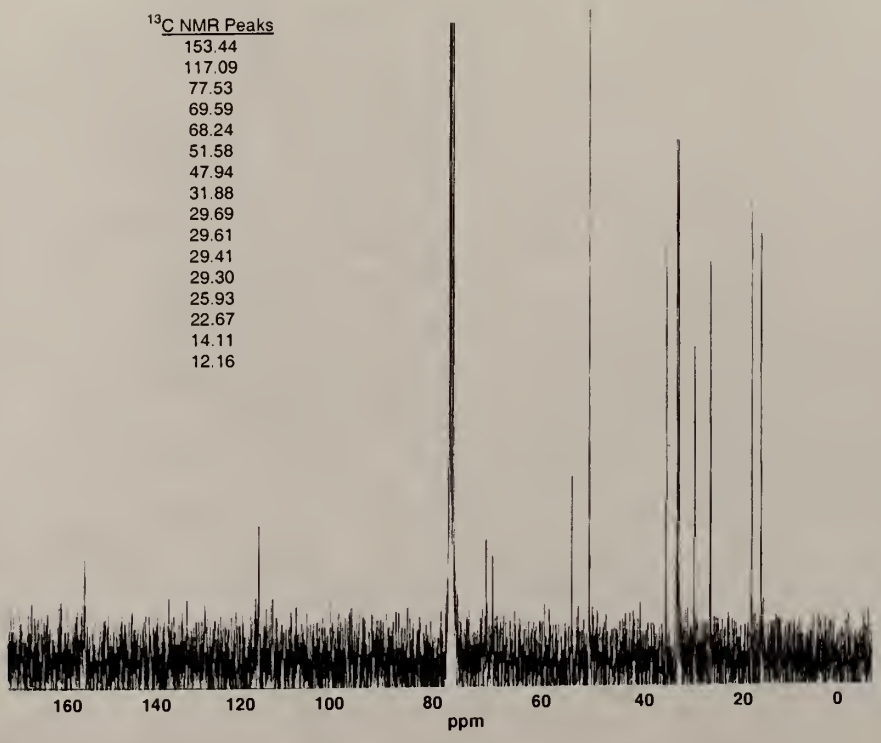


Figure 4-15. ^{1}H and ^{13}C NMR of **PPE-NEt$_2$/OC9(20)[54]** in $CDCl_3$.

Based on the endcapped polymer repeat unit structure shown in Figure 4-15, the number of repeat units, n, can be calculated from ^{1}H NMR integration values using the formula:

$$\frac{4n+2}{4} = \frac{c}{a} = \frac{4.00}{0.17} \qquad (4\text{-}1)$$

where n = 23 (46 rings) or subsequently a $\overline{M}_n$ = 16,500 g/mol. It should be noted that this number is an approximation and several factors should be considered when using this approximation, such as possible errors in the NMR integration values and the presence of iodine (0.37%) in the sample, which indicates non-endcapped chain ends. Assuming a liberal estimation of these errors, it is safe to assume that minimally a DP = 15 ($\overline{M}_n$ = 10,000 g/mol; 30 rings) has been achieved.

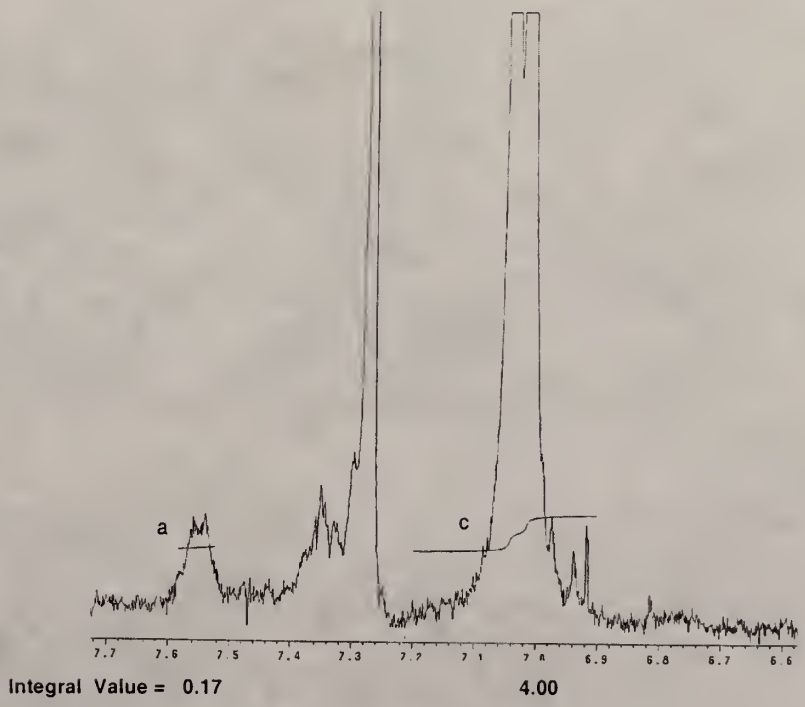


Figure 4-16. Expansion of the aromatic region of the ^{1}H NMR of **PPE-NEt$_2$/OC9(20)[54]** in $CDCl_3$.

Polymer Quaternization

Figure 4-17 outlines two routes to synthesizing cationic polyelectrolytes from **PPE-NEt$_2$/OC9(20)[54]**. Direct treatment of the neutral polymer in EtOH with 1M HCl to lower pH and protonate the amine sites was a successful methodology to create a polyelectrolye, **PPE-NEt$_2$H+/OC9(20)[55]** that was soluble in the lowered pH ethanol and displayed interesting physical properties different from the neutral version (to be discussed in Physical Properties section). Unfortunately, the **PPE-NEt$_2$H+/OC9(20)[55]** was not soluble in lowered pH water alone, but required the addition of ethanol or 2-propanol to dissolve. Solutions of the neutral polymer in lowered pH ethanol were cast onto Teflon® and could be removed as free standing thin films. The solutions also have the capability to be directly used in electrostatic deposition experiments and avoid the added synthetic step of quaternization with bromoethane and its difficulties to be described below.

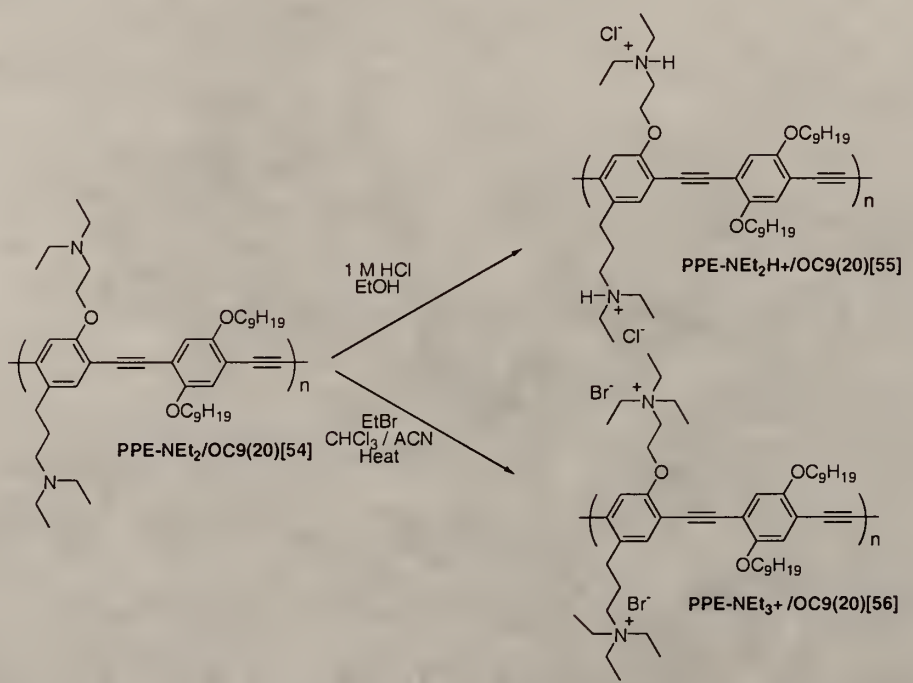


Figure 4-17. Conversion of **PPE-NEt$_2$/OC9(20)[54]** to cationic polyelectrolytes.

Treatment of **PPE-NEt$_2$/OC9(20)[54]** in a 50 ^{0}C chloroform/acetonitrile solution with bromoethane to synthesize **PPE-NEt$_3$+/OC9(20)[56]** promoted the agglomeration and subsequent insolubility seen in previously mentioned neutral polymer syntheses. After 3 days of reaction time, a swollen orange material precipitated from the reaction medium. The solution was concentrated and added to an excess of THF. An orange material was collected via filtration, which was poorly soluble in ethanol and insoluble in other organic solvents and water. Lowering of the pH of the ethanol solution did not promote any extra solubility. Elemental analysis revealed a 12.58% bromine content by weight indicating a 73% quaternization efficiency. The lowered efficiency as compared to previously described PPP and PPT polyelectrolytes is most likely a result of the precipitation of the polymer during the reaction and/or its strong agglomeration and packing. The lowered number of quaternized sites cannot, in itself, account for the poor solubility in EtOH since lowering the pH should protonate any non-quaternized sites, thus making the polymer soluble in EtOH. The small amount of quaternized polymer that was soluble in EtOH displayed an optical absorbance very similar to that of the **PPE-NEt$_2$H+/OC9(20)[55]** which will be discussed in detail in the Physical Properties section. Based on these observations and results, it was determined that **PPE-NEt$_2$H+/OC9(20)[55]** could be used as an effective alternative to a bromoethane quaternized polyelectrolyte and therefore the properties of **PPE-NEt$_2$H+/OC9(20)[55]** were investigated more fully than those of the **PPE-NEt$_3$+/OC9(20)[56]** material.

Physical Properties of PPE Type Polymers

Figure 4-18 shows the UV-Vis absorbance and photoluminescence spectra for **PPE-NEt$_2$/OC9(20)[54]** in $CHCl_3$ and **PPE-NEt$_2$H+/OC9(20)[55]** in low pH EtOH

(normalized for convenience). It is interesting to note the dramatic shift in absorbance maximum between the neutral and charged polymers. **PPE-NEt_2/OC9(20)[54]** exhibits a λ_{max} at 442 nm with a corresponding molar absorptive of about 43,000 L $mol^{-1}cm^{-1}$, while **PPE-NEt_2H+/OC9(20)[55]**'s λ_{max} is blue shifted 34 nm to 408 nm with a corresponding molar absorptivity of about 110,000 L $mol^{-1}cm^{-1}$. Fine tuning of the λ_{max} in solution could be achieved by controlling the pH of the solution (assuming that polymer solubility in a suitable solvent can be maintained), as incomplete prolongation would lead to a lower extent of hypsochromic shift.

The solution emission results revealed a dramatic increase in the emission intensity for the protonated polymer when compared to the neutral PPE, much like that seen in Chapter 2 for the **PPP-NEt** polymers. Quantum yields were obtained for each polymer relative to perylene with a quantum yield of 0.94 revealing a value of only 0.001 for **PPE-NEt_2/OC9(20)[54]** and a dramatic increase to 0.86 for the protonated **PPE-NEt_2H+/OC9(20)[55]**. Each polymer has a blue-green solution luminescence at 502 nm for **PPE-NEt_2/OC9(20)[54]** and 464 nm for **PPE-NEt_2H+/OC9(20)[55]**. The increase in quantum yield is attributed to the prevention of quenching of the excited state by the lone pair of electrons on the nitrogen by protonation. The dramatic change in emission when the amine sites are "protected" makes these polymers excellent candidates for H^+ or alkylating agent sensors. Table 4-2 summarizes the optical properties for the **PPE-OC9(20)** polymers.

Table 4-2. Summary of optical data for **PPE-OC9(20)** type polymers.

Polymer	Absorbance λ_{max} (nm)	Film Color	Emission λ_{max} (nm)	Emission Color (Solution)	Quantum Yield
PPE-NEt_2 /OC9(20) [54]	442	Orange	502	Blue-Green	0.001
PPE-NEt_2H+ /OC9(20) [55]	408	Orange	464	Blue-Green	0.86

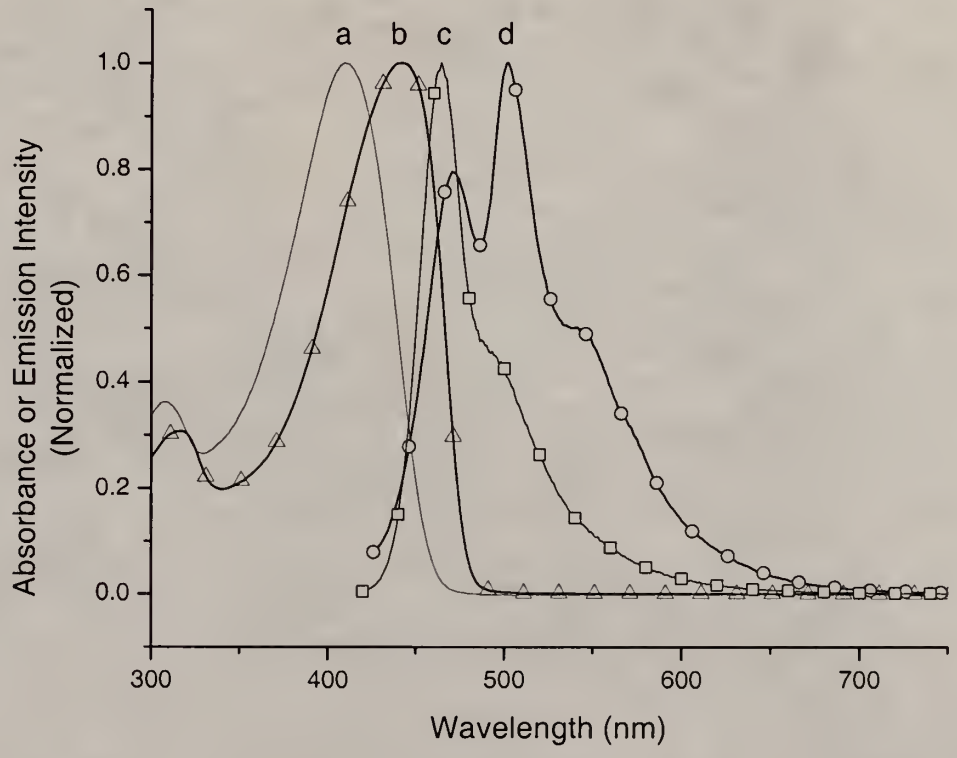


Figure 4-18. Normalized UV-Vis absorption and solution photoluminescence for **PPE-OC9(20)** type polymers.

a) **PPE-NEt_2H+/OC9(20)[55]** UV-Vis absorption in EtOH.
b) **PPE-NEt_2/OC9(20)[54]** UV-Vis absorption in $CHCl_3$.
c) **PPE-NEt_2H+/OC9(20)[55]** emission in EtOH.
d) **PPE-NEt_2/OC9(20)[54]** emission in $CHCl_3$.

Thermal de-protonation of the amine sites can occur if the polymer is exposed to elevated temperatures, thus indicating a dynamic equilibrium at the amine sites. This de-protonation is evidenced in the TGA for **PPE-NEt$_2$H+/OC9(20)[55]** shown in Figure 4-19 where an initial degradation event starting at 188 ^{0}C is observed (loss of HCl), followed by a steady decline in weight (20 weight% remaining @ 522 ^{0}C). The initial weight loss event in the degradation of **PPE-NEt$_2$/OC9(20)[54]** occurs slightly higher at 210 ^{0}C followed by a steady decline in weight (20 weight% remaining @ 625 ^{0}C). Both polymers are completely degraded by a temperature of 700 ^{0}C.

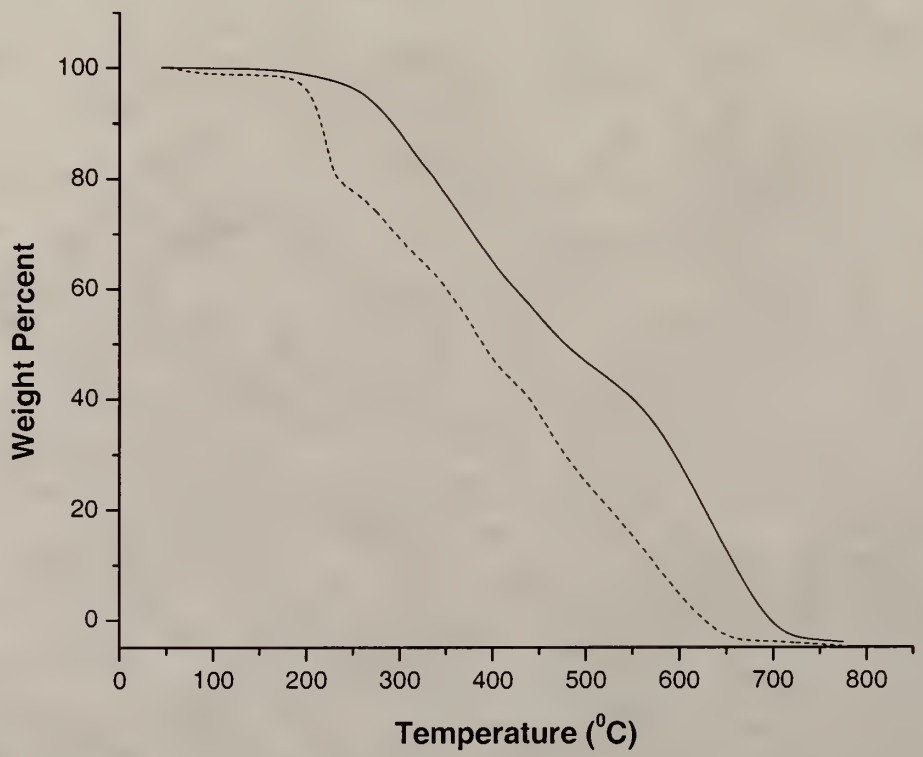


Figure 4-19. TGA thermograms for neutral and protonated **PPE-OC9(20)** under N_2.
a) —— **PPE-NEt$_2$/OC9(20)[54]** neutral
b) ----- **PPE-NEt$_2$H+/OC9(20)[55]** protonated

Conclusions

An interesting cationic poly(*p*-phenyleneethynylene) (**PPE-NEt_2H+/OC9(20)[55]**) has been synthesized by application of the Heck-Cassar-Sonogashira-Hagihara reaction. Using this reaction, very high molecular weight species can be synthesized, aided by the precipitation of amine salts, which drive the polymerization to completion. With the high rigidity and solubility issues of these PPE systems, oftentimes it is more fruitful to limit molecular weight with endcapping agents to improve solubility and aid in molecular weight determination via ^{1}H NMR analysis. The use of $Pd(PPh_3)_4$ as catalyst helps avoid stoichiometric imbalance problems that can occur with monomer equivalencies when Pd(II) catalysts are used, but special care must be taken in the handling of the air sensitive catalyst.

Using the conditions described in this chapter and the experimental section in Chapter 5, the neutral polymer **PPE-NEt_2/OC9(20)[54]** was isolated in nearly quantitative yield, with special care taken to ensure the polymer chains did not aggregate and decrease solubility post-precipitation. A number average molecular weight of 16,500 g/mol was estimated by ^{1}H NMR, corresponding to a degree of polymerization of 23. GPC determinations of polydispersity and molecular weights were unsuccessful at this time due to several factors. Optical data have shown that the polymers emit in the blue-green region of the visible spectrum in solution and the solution quantum yield improves from 0.001 to 0.86 in the case of the neutral compared to the protonated polymer.

These results have open the door for continued research in PPE polymers for the Reynolds' research group. Using the experimental protocols outlined in this chapter, future workers can further modify the PPE backbone structures to improve solubility

(with the use of other bulky "bis" substituents such as 2-ethylhexyl) and/or create interesting new materials, especially with the syntheses outlined in Figures 4-9 through 4-12. Furthermore, the length of the carbon spacing in the starting material **42** could be adjusted to ultimately provide PPE's with active endgroups at differing lengths from the conjugated polymer backbone. Such materials would be interesting for possible surface adsorption studies or energy transfer studies to metallated species covalently attached to the chain ends.

CHAPTER 5
CONCLUSIONS

Polymer chemistry and science, once thought of as merely a grafted branch onto the tree of traditional chemistries (organic, inorganic, physical), has taken its place as a fundamental science over the past decades. The "tree" of polymer chemistry will always be rooted in the above mentioned chemical divisions, but it has grown to unexpected heights on its own merits and branched into fields of study hitherto unforeseen. It is fitting that many of today's most advanced research efforts are now using polymer science as the foundation of growth, while trying to add traditional chemical and biochemical functionalities to the macromolecular design. As control over supramolecular shapes and folding, like that seen in proteins, advances one can only imagine the structure/property relationships that will become available during the next decades.

One of the largest fields of current study is in the field of electroactive polymers, which display remarkable optical and conductive properties when potentials are applied. The focus of this dissertation is to shed light on the synthesis, stability, and basic optical properties of a series of conjugated polyelectrolytes. These unique conjugated polymers not only have interesting optical properties, but are of interest in basic polymer science for the study of the effects of the rigid backbone versus that of the pendant side chain charges on the polymer shape ("polyelectrolyte effect"). Using Suzuki, Stille, and Sonogashira type Pd(0) cross-coupling reactions, a series of three different polymer

backbones were synthesized [poly(*p*-phenylene), poly(*p*-pheneylene-*co*-thiophene), and poly(*p*-pheneyleneethynylene)], each with its own distinguishing physical, chemical, and optical properties.

Chapter 2 of this dissertation presents the experimental work on the poly(*p*-phenylene) derivatives (**PPP-NEt$_2$**) which contain alkoxy-amine side chains that can be quaternized or protonated to generate water soluble polymers that emit blue light. Initial work conducted by Dr. Peter Balanda was expanded upon to allow for scale up production and elimination of contamination by precipitated Pd(0) metal into the polymer. Modified Suzuki polymerization protocols were employed in the various **PPP-NEt$_2$** syntheses to couple bis(neopentylglycol)-1,4-phenylenediboronate with 2,5-bis(3-[*N,N*-diethylamino]-1-oxapropyl)-1,4-diiodobenzene (**DINEt**). The use of $PdCl_2$(dppf) catalyst was a success in achieving the desired goals as a polymer, **PPP-NEt$_2$(dppf)[12]**, of $\overline{M}_n$ = 18,700 g/mol and polydispersity of 1.18 based on GPC results versus polystyrene standards was recovered from multi-gram scale reactions without contamination from black Pd(0).

Several key synthetic insights were also gained from the work concerning the nature of the halogenated monomer and solvent choice. Iodinated monomers were found to react the fastest, but ultimate polymer molecular weights were very similar to polymerizations conducted with brominated monomers. This result is due to the precipitation of the polymer during the coarse of reaction, thereby terminating chain growth based on solubility limits. The polar solvents THF and DMF with added water were the most effective solvents compared to acetone, methanol, or toluene.

Solution absorbance of the bromoethane quaternized derivative (**PPP-NEt_3+[19]**) in water occurred at 330 nm with corresponding photoluminescent emission at 410 nm. The tan polymeric material could be easily manipulated into thin multi-layer LED devices using an electrostatic adsorption technique. Thermogravimetric analysis of the quaternized polymer revealed an initial weight loss at 230 ^{0}C due to the loss of bromoethane and a subsequent triethylamine fragment as the side chains were cleaved with heating under N_2.

The next progression in the research was to lower the energy of the emission by incorporation of thiophene units into the polymer backbone. Ideally, this could be achieved using a similar Suzuki reaction as that used for the PPP's. Experimentation revealed that use of a 2,5-thiophene diboronate ester in a Suzuki polymerization was ineffective for the production of polymeric materials as the boronate functional groups on thiophene are much more susceptible to hydrolysis and decomposition than those on phenylene used for the PPP synthesis. A Stille coupling methodology was employed and it was determined that dropwise addition of 2,5-bis(trimethylstannyl)thiophene to **DINEt** in DMF with $PdCl_2(PPh_3)_2$ catalyst produced the highest molecular weight polymer,**PPT-NEt_2(96-drop)[28]**, with a $\overline{M}_n$ = 5,300 g/mol and polydispersity of 1.7. The somewhat lower molecular weight can be attributed to the lower reactivity of the tin reagents used in the Stille reaction as compared to the boronic reagents used in the Suzuki reaction and possible methyl transfer from the 2,5-bis(trimethylstannyl)thiophene which would endcap the polymer and terminate chain extension.

The water soluble derivative formed by treatment of the neutral polymer with bromoethane, **PPT-NEt_3+(96-drop)[31]**, had a solution absorbance in water at 411 nm

with a corresponding photoluminescent emission at 494 nm, placing the emission in the blue-green region of visible light. The PPT polymers were slightly less thermally stable than the PPP polymers, with initial degradation events under N_2 occurring at 200 ^{0}C. Unfortunately, the use of **PPT-NEt$_3$+(96-drop)[31]** in electroluminescent devices appears unlikely as initial data from collaborative efforts have indicated very low emission from thin layer devices. Unexpectedly, a promising application of the polymer has arisen involving the use of **PPT-NEt$_3$+(96-drop)[31]** in electrostatically deposited thin layer systems for control over refractive index properties. Research is currently ongoing with collaborators at MIT to uncover the exact nature and behavior of these adjustable refractive index behaviors.

With the emission properties of the PPT polymers not meeting expectations, an alternative blue-green emitting system was desired. Incorporation of ethynylene linkages into the polymer backbone also lowers the energy of emission as compared to PPP. Several experimental concepts were employed as the Sonogashira polymerization was fine-tuned to produce the best polymer for the applications needed. The Sonogashira reaction is an excellent polymerization route as the amine salt by-products that are formed during the coarse of the reaction precipitate and help drive the reaction to completion. The highly rigid nature of poly(*p*-pheneyleneethynylene) makes solubility issues crucial when designing the polymer. It was found that controlling molecular weight via endcapping to a degree of polymerization of approximately 20 when reacting 1,4-diethynyl-2,5-bis(nonyloxy)benzene with **DINEt**, along with careful precipitation and drying, was critical in isolation a soluble neutral polymer. A number average molecular weight of 16,500 g/mol was estimated by ^{1}H NMR, corresponding to a degree

of polymerization of 23 (46 rings). GPC determinations of polydispersity and molecular weights were unsuccessful at this time due to polymer interactions with the column packing material.

The neutral PPE type polymer, **PPE-NEt_2/OC9(20)[54],** could be dissolved in organic solvents and dramatically increased emission was observed when the polymer was dissolved in ethanol of lowered pH, **PPE-NEt_2H+/OC9(20)[55]**. The acidic solution protonates the amine sites and prevents quenching of the fluorescence by the lone pair of electrons on the free amine. Optical data have shown that the polymers emit in the blue-green region of the visible spectrum in solution (464 nm) and the solution quantum yield improves from 0.001 to 0.86 in the case of the neutral compared to the protonated polymer. Thermal degradation of **PPE-NEt_2H+/OC9(20)[55]** was initiated at 188 ^{0}C under N_2 (loss of HCl) followed by a steady decline in weight (20% weight % left at 522 ^{0}C). Complete degradation occurs by a temperature of 700 ^{0}C. Treatment of the neutral polymer with bromoethane promoted insolubility of the resulting partially quaternized polymer and was thus ineffective in producing a useful polyelectrolyte.

Taking into account the discoveries and observations made over the coarse of the graduate research, it becomes only natural to look at which facets of the research should continue in order to produce the most impact for future endeavors. This dissertation frames the synthetic protocols of a variety of Pd(0) polymerizations with the methodologies explained in a manner that can only be gained from hands-on experimentation. The insights should be invaluable to future students in the Reynolds' research group to construct conjugated polymers not even envisioned at this point. More direct in nature, future work could extend the experimental procedures to construct a

complete set of conjugated polyelectrolytes with bandgaps that vary over lower visible energy regions, such as addition of an alkoxy-amine substituted poly(*p*-phenylenevinylene). Polymers tailored with specific energy absorptions and emissions that could transfer energy to specific metal centers could easily be designed for sensing or charge transfer studies. The guidelines future workers should follow are simple: determine the properties needed, which type of conjugated polymer will meet the need, and perform reactions!

CHAPTER 6
EXPERIMENTAL

Reagents and Solvents. All reagents and solvents were purchased from Aldrich or Fisher unless otherwise noted. Pd catalysts were purchased exclusively from Strem Chemical. 1,4-Dibromobenzene and 4,4'-dibromobiphenyl (Aldrich) were recrystallized from hot pentane and toluene. Tetrahydrofuran (THF), toluene, and diethyl ether used in Grignard, alkyllithium, or polymerization reactions were distilled from Na/K allow. Anhydrous DMF and diisopropylamine were purchased from Aldrich. The diboronic esters, **8** and **9**, were synthesized by *in situ* transesterification with neopentyl glycol of the diboronic acids made by literature methods.[63]

General Methods. NMR spectra were obtained with a Varian VXR-300 or a Varian Gemini-300. Elemental analyses were performed by Robertson Microlit, Inc. or in house by combustion with a Fisons/Carlo-Erba 1106 and 1108. Ultraviolet-visible (UV-Vis) spectra were recorded using a Varian Cary 5E UV-Vis-NIR spectrophotometer with measurements taken as the average of three separate samples for the molar absorptivies data presented for polymers. Fluorescence results were obtained with a Spex F-112 photon counting fluorimeter at room temperature. TGA was performed under N_2 with a Perkin-Elmer TGA 7 Thermogravimetric Analyzer at 10°C per minute under N_2 atmosphere. GPC results were obtained with a system consisting of a Waters Model 590 pump, two 300 x 7.5 mm Polymer Laboratories Linear Mixed Bed (Plgel 5μm mixed-C) columns in series and using a Spectraflow 757 Tunable UV-Vis Detector. Gas chromatography measurements were performed on a Shimadzu GC-17A utilizing a 15

meter long Restek Corporation RTX-5 crossbond 5% diphenyl-95% dimethylsiloxane column. The heating profile used consisted of holding at 50^{0}C for 3 minutes, heating to 275 ^{0}C at a rate of 10 ^{0}C per minute, and holding at the final temperature for 2 minutes prior to cooling.

Chapter 2

2,5-dimethoxy-1,4-diiodobenzene (5). A 250 mL, 3 neck round bottom flask was charged with 1,4-dimethoxybenzene (**4**) (10.48 g, 75.85 mmol) and a solvent system consisting of 90:7:3 HOAc/ H_2O/ H_2SO_4 by volume. The reaction mixture was stirred under Ar until the 1,4-dimethoxybenzene dissolved completely. I_2 (23.66 g, 91.02 mmol) and KIO_4 (20.93 g, 91.02 mmol) were added and the reaction heated to 70 ^{0}C overnight. The reaction was cooled, poured into 500 mL H_2O, and a crude orange solid collected. The crude solid was recrystallized from THF/H_2O yielding a light yellow solid (24.03 g, 81% yield). mp 168-170 ^{0}C (lit. mp[105] 169 ^{0}C) ^{1}H NMR (300 MHz, $CDCl_3$) 7.20 (s, 2 H), 3.83 (s, 6 H) ppm. ^{13}C NMR (75.5 MHz, CDCl3) 153.29, 121.57, 85.44, 57.17 ppm. Anal. Calcd for $C_8H_8O_2I_2$: C, 24.62; H, 2.05. Found: C, 24.31; H, 1.89. EI-LRMS calculated for $C_8H_8O_2I_2$: 389.9, Found 390.

2,5-diiodohydroquinone (DIHQ). 2,5-dimethoxy-1,4-diiodobenzene (10.00 g, 25.60 mmol) was dissolved in 50 mL dichloromethane and cooled in a dry ice/acetone bath. Boron tribromide (26.50 g, 105.80 mmol) in 15 mL dichloromethane was added dropwise via an addition funnel to the solution with stirring. The reaction mixture was held at –78 ^{0}C for 30 min and then allowed to warm to room temperature overnight. The reaction was added slowly to 300 mL of ice water. A brown precipitate was collected and recrystallized from THF / H_2O leaving a white crystalline material (7.05 g, 76%

yield). mp 192-193 ^{0}C (lit. mp.[62] 192 – 194 ^{0}C). ^{1}H NMR (300 MHz, acetone-d_6) 8.75 (s, 2 H), 7.30 (s, 2 H) ppm. ^{13}C NMR (75 MHz, acetone-d_6) 151.58, 124.93, 84.25 ppm. Anal. Calcd for $C_6H_4O_2I_2$: C, 19.90; H, 1.11. Found: C, 19.73; H, 1.08. EI-LRMS calculated for $C_6H_4O_2I_2$: 361.8, Found 362.

2,5-Dibromohydroquinone (DBHQ). A 2 liter, 3 neck round bottom flask equipped with magnetic stir bar, addition funnel, and nitrogen gas inlet and outlet tubing was charged with 500 mL of glacial acetic acid and 500 mL of methylene chloride. Hydroquinone (**6**) (30.00 g, 273.7 mmol) was added and remained undissolved. With vigorous stirring, 2.1 eq. of Br_2 (91.64 g, 572.2 mmol) was slowly added to the reaction flask from the addition funnel. Upon addition of the first equivalent of Br_2, the monobrominated species became soluble in the acetic acid / methylene chloride system. After the addition of 1 equivalent of Br_2 was complete, the dibromated compound began to precipitate from the solution as a pale pink solid. After total addition of the Br_2, the mixture was stirred for 3 hours. During the reaction, a slow stream of nitrogen was passed over the reaction and vented to a bath of aqueous sodium hydroxide to neutralize the HBr gas being liberated from the large scale reaction. The crude product was isolated by filtration and purified by recrystallization from a 5:1 (v/v) ispropanol / water solution. A white crystalline solid was recovered (29.34 g, 40% yield). mp 184-185 ^{0}C (lit. mp.[106] 185 - 186 ^{0}C). ^{1}H NMR (300 MHz, DMSO-d_6) 9.81 (s, 2 H), 7.01 (s, 2 H) ppm.

2,5-bis(3-[*N,N*-diethylamino]-1-oxapropyl)-1,4-diiodobenzene (DINEt). A 3 neck round bottom flask was equipped with a reflux condenser and Ar gas inlet. 2,5-diiodohydroquinone (6.45 g, 17.82 mmol), 2-chlorotriethylamine hydrochloride (**7**) (6.75 g, 39.21 mmol), and K_2CO_3 (10.33 g, 74.85 mmol) were added to the reaction flask. 150

mL of acetone (dried over $MgSO_4$) was added and the reaction stirred and refluxed. After 3 days, a yellow slurry was poured into 300 mL of H_2O and a solid precipitate collected. The filtrate was extracted with Et_2O (300 mL x 1, 150 mL x 1, 50 mL x 1). The solid precipitate was dissolved in Et_2O and the organics combined. The combined Et_2O layers were washed with 1M NaOH (300 mL x 1, 150 mL x 1, 50 mL x 1), H_2O (300 mL x 1), and brine (300 mL x 1). The Et_2O layer was dried over $MgSO_4$ and the solvent removed under reduced pressure leaving a yellowish white solid. The solid was recrystallized twice from MeOH / H_2O (7.49 g, 75% yield). mp 79-80 ^{0}C. ^{1}H NMR (300 MHz, $CDCl_3$) 7.21 (s, 2 H), 4.00 (t, J = 6.0 Hz, 4 H), 2.91 (t, J, = 6.0Hz, 4 H), 2.66 (q, J = 7.2 Hz, 8 H), 1.08 (t, J = 7.2 Hz, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 152.84, 122.82, 86.02, 69.20, 51.49, 47.92, 12.09 ppm. Anal. Calcd for $C_{18}H_{31}N_2O_2I_2$: C, 38.59 ; H, 5.40 ; N, 5.00; I, 45.30. Found: C, 38.81; H, 5.53; N, 4.90; I, 45.10. FAB-HRMS (M + H)$^+$ calculated for $C_{18}H_{31}N_2O_2I_2$: 561.0475, Found 561.0492.

2,5-Bis(3-[*N,N*-diethylamino]-1-oxapropyl)-1,4-dibromobenzene (DBNEt). A 500 mL round bottom flask with magnetic spin bar and reflux condenser was charged with anhydrous potassium carbonate (72.0 g, 521 mmol), 2-chlorotriethylamine hydrochloride (**7**) (22.56 g, 131 mmol), 2,5-dibromohydroquinone (**DBHQ**, 13.46 g, 50.2 mmol), and 300 mL acetone (dried over $MgSO_4$ previously). The reaction was brought to reflux for three days. The reaction mixture was diluted with 300 mL water, dissolving all salts. The product was extracted with ether (1 x 300, 2 x 200 mL) and the combined organics washed with 1M NaOH (aq.) (2 x 100 mL), water (2 x 200 mL) and brine (1 x 200 mL). The solution was dried over $MgSO_4$, filtered and stripped of solvent by vacuum evaporation to yield crude oily solids. The crude product was recrystallized from

MeOH/H_2O twice to give white microcrystalline product which was dried *in vacuo* over $CaSO_4$. Yield 8.89 g [38 %], mp 76-78°C. ^1H NMR (300 MHz, $CDCl_3$) ppm. 7.12 (s, 2 H), 4.05 (t, J = 5.4 Hz, 4 H), 2.75 (t, J = 5.8 Hz, 4 H), 2.34 (s, 12 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$) 150.55, 119.37, 111.61, 69.39, 58.18, 46.02 ppm. Anal. calcd for $C_{14}H_{22}N_2O_2Br_2$: C, 41.00; H, 5.41; N, 6.83. Found: C, 41.13; H, 5.44; N, 6.71.

1,4-Diphenyl-2,5-bis(3-[*N,N*-diethylamino]-1-oxapropyl)phenylene (10). A 150 mL side arm vacuum flask with magnetic stir bar was flame dried under vacuum and backfilled with Ar gas. 50 mL of DMF and 10 mL of H_2O were added and sparged with Ar for 30 min. **DINEt** (0.80 g, 1.4 mmol), phenylboronic acid (0.40 g, 3.3 mmol), and $NaHCO_3$ (84.0 g, 14.0 mmol) were added and allowed to dissolve. $PdCl_2$(dppf) (0.030 g, 0.04 mmol) was added in one portion and the reaction stirred with heating to 50 ^{0}C for 12 hours. After cooling, 50 mL of Et_2O and H_2O each were added and the organic fraction collected. The aqueous layer was extracted with Et_2O (2 x 50 mL) and the combined organics were washed with 1M NaOH (3 x 50 mL), H_2O (3 x 50 mL), and finally with brine (1 x 100 mL). The organics were dried over $MgSO_4$, and the solvent removed under vacuum revealing a yellowish white solid. The product was dissolved in THF and filtered through a plug of silica gel to remove catalyst contamination. After removal of solvent, a white solid was recovered. Yield 0.449 g [68 %]. ^1H NMR (300 MHz, $CDCl_3$) ppm. 7.58 (d, J = 6.6 Hz, 4 H), 7.39 (t, J = 7.1 Hz, 4 H), 7.32 (d, J = 7.1 Hz, 2 H), 6.98 (s, 2 H), 3.97 (t, J = 6.0 Hz, 4 H), 2.75 (t, J = 6.0 Hz, 4 H), 2.50 (q, J = 7.1 Hz, 8 H), 0.95 (t, J = 7.1 Hz, 12 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$) 129.55, 127.90, 126.91, 116.63, 68.74, 52.06, 47.81, 12.03 ppm. Anal. calcd for $C_{30}H_{40}N_2O_2$: C, 78.21;

H, 8.76; N, 6.08. Found: C, 78.41; H, 9.56; N, 5.90. FAB-HRMS (M^+) calculated for $C_{30}H_{40}N_2O_2$: 460.3090, Found 460.3111.

1,4-Diphenyl-2,5-bis(3-[*N,N,N*-triethylammonium]-1-oxapropyl)phenylene dibromide (11). Compound **7** (0.22 g, 0.5 mmol) was dissolved in THF and stirred with 15 mL of bromoethane for 2 days. The solution became cloudy during the course of the reaction. A white solid (0.21 g, 0.3 mmol) was collected by precipitation into hexane and dried *in vacuo* overnight. The new material was highly soluble in acetonitrile and water indicating a successful reaction of the neutral compound **10**. Yield 0.210 g [65%]. ^1H NMR (300 MHz, D_2O) ppm. 7.27 (bm, 4 H), 6.82 (s, 2 H), 4.00 (t, J = 4.2 Hz, 4 H), 3.25 (t, J = 4.2 Hz, 4 H), 2.91 (q, J = 7.2 Hz, 12 H), 0.95 (t, J = 7.2 Hz, 18 H) ppm. Anal. calcd for $C_{34}H_{50}N_2O_2Br_2$: C, 60.34; H, 7.45; N, 4.14; Br, 23.34. Found: C, 61.27; H, 7.67; N, 4.29; Br, 22.54. FAB-HRMS (M^+) calculated for $C_{34}H_{50}N_2O_2Br_2$: 676.2239, Found 676.2965

General Procedure for Suzuki Polymerization Preparation of Poly({2,5-bis[2-(*N,N*-diethylamino)-1-oxapropyl]-1,4-phenylene}-*alt*-1,4-phenylene) [PPP-NEt_2]. Organic solvent and H_2O (5:1 v/v) were sparged with argon for 1 hour. A Schlenk flask with a magnetic spin bar was charged with **DBNEt** or **DINEt**, bisneopentylglycol 1,4-phenylenediboronate (**8**), carbonate base, and Pd (II) catalyst. The flask was evacuated and backfilled with argon three times. The solvent was added via cannula to the flask and the reaction was heated to 75°C and stirred for an appropriate amount of time. The solution was precipitated into 200 mL of cold methanol and collected on a glass frit. The polymer was washed with methanol then water, dried in an air stream, then dried *in vacuo* at 60°C overnight. NMR and optical data that are identical for all PPP-NEt_2

samples are listed below. ^{1}H NMR (300 MHz, $CDCl_3$) 7.71 (bm, 4 H), 7.13 (bm. 2 H), 4.11 (bm, 4 H), 2.87 (bm, 4 H), 2.62 (bm, 8 H), 1.05 (bm, 12 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$) 150.41, 136.98, 130.53, 129.10, 116.32, 68.32, 51.98, 47.82, 12.03 ppm . UV-Vis (THF) λ_{max} = 350 nm, log ε_{max} = 3.84; λ_{max} = 290 nm, log ε_{max} = 3.74. UV-Vis (1M HCl) λ_{max} = 352 nm, log ε_{max} = 3.98; 290 nm, log ε_{max} = 3.64. PL (THF with 370 nm excitation) λ_{max} = 435 nm. PL (1 M HCl with 370 nm excitation) λ_{max} = 408 nm.

PPP-NEt$_2$ (Br-72)[14]. Reagents: **DBNEt** (0.976 g, 2.09 mmol), bisneopentylglycol 1,4-phenylenediboronate (**8**, 0.632 g, 2.09 mmol), Na_2CO_3 (1.33g, 12.56 mmol), and $Pd(OAc)_2$ (20 mg, 4 mol %). 25 mL DMF and 5 mL H_2O were used as solvent. Reaction time: 3 days. Yield: 0.61 g [76 %]. Anal. calcd for $C_{24}H_{34}N_2O_2Br_{0.026}$: C, 74.95; H, 8.91; N, 7.28; Br, 0.53. Found: C, 75.09; H, 8.92; N, 8.05; Br, 0.54. GPC ($CHCl_3$ vs. PS) $\overline{M}_n$ = 15,900 gmol^{-1}, *MP* = 24,300 gmol^{-1}, $\overline{M}_w$ = 35,000 gmol^{-1}, $\overline{M}_w/\overline{M}_n$ = 2.20.

PPP-NEt$_2$ (dppf)[12]. Reagents: **DBNEt** (1.995 g, 4.28 mmol), bisneopentylglycol 1,4-phenylenediboronate (**8**, 1.293 g, 4.28 mmol), $NaHCO_3$ (3.60 g, 42.86 mmol), and $PdCl_2$(dppf) (35 mg, 1 mol %) [Strem Chemicals Inc.]. 50 mL DMF and 10 mL H_2O were used as solvent. Reaction time: 3 days. Yield: 1.552 g [95 %]. Anal. calcd for $C_{24}H_{34}N_2O_2Br_{0.026}$: C, 74.95; H, 8.91; N, 7.28; Br, 0.53. Found: C, 75.21; H, 8.94; N, 8.01; Br, 0.45. GPC ($CHCl_3$ vs. PS) $\overline{M}_n$ = 18,700 gmol^{-1}, *MP* = 19,400 gmol^{-1}, $\overline{M}_w$ = 22,100 gmol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.18.

PPP-NEt$_2$(I-3)[15]. Reagents: **DINEt** (1.0189 g, 1.819 mmol), bisneopentylglycol-1,4-phenylene diboronate (**8**, 0.5492 g, 1.819 mmol), Na_2CO_3 (1.93 g, 18.21 mmol), and $Pd(OAc)_2$ (6.73 mg, 0.03 mmol) 25 mL DMF and 5 mL H_2O were used as solvent. Reaction time: 3 hours. Yield: 0.50 g [72 %]. Anal. calcd for $C_{24}H_{34}N_2O_2I_{0.045}$: C, 74.24; H, 8.42; N, 7.22; I, 1.47. Found: C, 67.32; H, 8.42; N, 6.01; I, 1.48. GPC ($CHCl_3$ vs. PS) $\overline{M}_n$ = 10,900 g mol^{-1}, *MP* = 13,300 g mol^{-1}, $\overline{M}_w$ = 16,600 g mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.52.

PPP-NEt$_2$ (I-24)[16]. Reagents: **DINEt** (0.9589 g, 1.712 mmol), bisneopentylglycol-1,4-phenylene diboronate (**8**, 0.5169g, 1.712 mmol), Na_2CO_3 (1.81g, 17.12 mmol), and $Pd(OAc)_2$ (6.73 mg, 0.03 mmol) 25 mL DMF and 5 mL H_2O were used as solvent. Reaction time: 24 hours. Yield: 0.52 g [80 %]. Anal. calcd for $C_{24}H_{34}N_2O_2I_{0.023}$: C, 74.82; H, 8.83; N, 7.27; I, 0.76. Found: C, 71.85; H, 8.45; N, 6.78; I, 0.77. GPC ($CHCl_3$ vs. PS) $\overline{M}_n$ = 15,300 g mol^{-1}, *MP* = 19,500 g mol^{-1}, $\overline{M}_w$ = 27,500 g mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.80.

Poly({2,5-bis[2-(*N,N*-diethylamino)-1-oxapropyl]-1,4-phenylene}-*alt*-4,4'-biphenylene) [PPPBP-NEt$_2$[13]]. 50 mL of THF and 10 mL of H_2O were sparged with argon under reflux for 1 hour. A 200 mL Schlenk flask with a magnetic spin bar was charged with **DBNEt** (0.5975 g, 1.28 mmol), bisneopentylglycol 4,4'-diphenylenediboronate (**9**, 0.4848 g, 1.28 mmol), $NaHCO_3$ (1.07 g, 12.74 mmol), and $PdCl_2$(dppf) (10 mg, 1 mol %) [Strem Chemicals Inc.]. The flask was evacuated and backfilled with argon three times. The THF/H_2O solvent solution was added via cannula to the flask and the reaction was heated to 75°C and stirred for 3 days. The solution was precipitated into 200 mL of cold methanol and collected on a glass frit. The polymer was

washed with methanol then water, dried in an air stream, then dried *in vacuo* at 60°C overnight. Yield: 0.2990 g [51 %]. Anal. calcd for $C_{30}H_{38}N_2O_2$: C, 78.60; H, 8.30; N, 6.11. Found: C, 70.25; H, 8.22; N, 5.75; Br, 1.21. ^{1}H NMR (300 MHz, $CDCl_3$) 7.72 (bm, 8 H), 7.10 (bm. 2 H), 4.10 (bm, 4 H), 2.83 (bm, 4 H), 2.55 (bm, 8 H), 1.00 (bm, 12 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$) 150.39, 137.58, 130.00, 126.66, 116.20, 68.38, 51.85, 47.76, 11.89 ppm. GPC ($CHCl_3$ vs. PS) $\overline{M}_n$ = 3,400 gmol^{-1}, *MP* = 5,300 gmol^{-1}, $\overline{M}_w$ = 8,900 gmol^{-1}, $\overline{M}_w/\overline{M}_n$ = 2.6 (GPC curve shape poor). UV-Vis (THF) λ_{max} = 350 nm, log ε_{max} = 3.98; λ_{max} = 290 nm, log ε_{max} = 3.70. PL (THF with 370 nm excitation) λ_{max} = 435 nm.

Quaternization of Polymeric Amino-Functionalized Poly(*p*-Phenylene)'s. Synthesis, percent yields, NMR, and optical transitions for all cationic **PPP-NEt$_3$+** samples were nearly identical, therefore, experimental details and characterization data are listed only for the quaternization of **PPP-NEt$_2$ (dppf)[12]** to the cationic, water soluble polymer.

Poly{2,5-bis[2-(*N,N,N*-triethylammonium)-1-oxapropyl]-1,4-phenylene-*alt*-1,4 phenylene} dibromide [PPP-NEt$_3$+[19]]. A 250 mL single neck round bottom flask with a magnetic spin bar was charged with **PPP-NEt$_2$ (dppf)[12]** (1.32 g, 3.46 mmol) and stirred at room temperature with bromoethane (5 mL) in THF (20 mL) in a sealed flask. The partially quaternized amine polymer **PPP-NEt$_3$+[19]** precipitated out of solution over the course of 5 days. The reaction was poured into acetone and a tan polymer collected on a medium porosity glass frit. Yield: 1.72 [83%]. ^{1}H NMR results. ^{1}H NMR (300 MHz, D_2O) 7.9-6.5 (bm, 6 H), 4.5-3.8 (bm, 4 H), 3.8-2.5 (bm, 16 H), 1.5-

0.4 (bm, 16.38 H [theo. 18 H]]) ppm. Anal. calcd for $C_{24}H_{34}N_2O_2 \cdot 1.6\ C_2H_5Br \cdot 2.54\ H_2O$: C, 54.02; H, 7.85; N, 4.63; Br, 21.48. Found: C, 52.35; H, 7.61; N, 4.31; Br, 21.40. UV-Vis (H_2O) λ_{max} = 330 nm, log ε_{max} = 4.17; λ_{max} = 282 nm, log ε_{max} = 4.02. PL (H_2O with 380 nm excitation) λ_{max} = 401 nm.

Poly{2,5-bis[2-(*N,N,N*-triethylammonium)-1-oxapropyl]-1,4-phenylene-*alt*-4,4'-biphenylene} dibromide [PPPBP-NEt$_3$+[20]]. A 250 mL single neck round bottom flask with a magnetic spin bar was charged with **PPPBP-NEt$_2$[13]** (0.20 g, 0.44 mmol) and stirred at room temperature with bromoethane (5 mL) in THF (20 mL) in a sealed flask. The partially quaternized amine polymer **PPPBP-NEt$_3$+[20]** precipitated out of solution over the course of 5 days. The reaction was poured into acetone and a tan polymer collected on a medium porosity glass frit. Yield: 0.25 g [85%]. Anal. calcd for $C_{34}H_{48}N_2O_2Br_2$: C, 60.27; H, 7.09; N, 4.14; Br, 23.63. Found: C, 65.68; H, 8.05; N, 5.35; Br, 11.98.

Chapter 3

2,5-bis(trimethylstannyl)thiophene (21). The general preparation of this compound followed literature procedures[81] followed by a more rigorous purification needed for polymerization quality monomer. The crude recovered product was distilled under vacuum (90 ^{0}C @ 5 x 10^{-3} mm Hg) and then recrystallized twice from pentane to yield a white crystalline solid. Yields for the reaction were slightly less than those reported in the literature due to the multiple purification steps employed (4.48 g, 69% yield). mp 100-102 ^{0}C (lit. mp.[81] 100-101.6 ^{0}C) ^{1}H NMR (300 MHz, $CDCl_3$) 7.40 (s, 2

H), 0.38 (s, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 143.00, 135.80, -8.15 ppm. Anal. Calcd for $C_{10}H_{20}SSn_2$: C, 29.32; H, 4.92. Found: C, 29.65; H, 4.60. FAB-HRMS $(M + H)^+$ calculated for $C_{10}H_{21}SSn_2$: 411.9330, Found 411.9494.

Thiophen-2,5-diyldiboronic acid (22). Magnesium (3.14 g, 129.16 mmol) was added to a 3 neck round bottom flask with reflux condenser and addition funned, flame dried under vacuum, and backfilled with Ar. 100 mL of dry THF was added to the flask. 2,5-dibromothiophene (14.88 g, 61.50 mmol) was dissolved in 50 mL of THF and added to the addition funnel. The dibromo solution was added slowly with stirring to the magnesium and brought to reflux for 5 hours after the addition was complete. The reaction was then cooled and chilled to –78 ^{0}C. Trimethyl borate (13.42 g, 129.16 mmol) was added dropwise to the Grignard reagent and allowed to warm to RT overnight. Et_2O was added (200 mL) and 1M HCl was added slowly to dissolve the Mg salts. The ether layer was collected and the aqueous layer extracted with ether (3 x 100 mL). The combined organics were evaporated leaving a smelly brown oil. The oil was successfully precipitated into 1M HCl and a solid collected. The solid was recrystallized from H_2O and 3.93 g of a white material was collected. (40% yield). ^{1}H NMR (300 MHz, DMSO-d_6) 8.14 (s, 4 H), 7.65 (s, 2 H) ppm.

Bis-2,2-dimethyltrimethylene thiophen-2,5-diyldiboronate (23). Thiophene-2,5-diyldiboronic acid (**22**) (4.69 g, 29.13 mmol), neopentylglycol (6.07 g, 58.26 mmol), and 150 mL of benzene were added to a 250 mL round bottom flask equiped with a Dean Stark trap and reflux condenser. The reaction was stirred and refluxed while the H_2O/benzene azeotrope was collected in the trap. After 24 hours the reaction was cooled, dried over $MgSO_4$, and the solvent removed by reduced pressure evaporation. A white

solid was recovered and recrystallized from hexane and a minimal amount of toluene (6.19 g, 70% yield). mp 158 ^{0}C (lit. mp.[63] 157-158 ^{0}C) ^{1}H NMR (300 MHz, $CDCl_3$) 7.57 (s, 2 H), 3.74 (s, 8 H), 1.00 (s, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 136.23, 72.34, 32.01, 21.90 ppm. Anal. Calcd for $C_{14}H_{22}O_4SB_2$: C, 54.52; H, 7.20. Found: C, 54.70; H, 7.14. FAB-HRMS $(M)^+$ calculated for $C_{14}H_{22}O_4SB_2$: 308.1425, Found 308.1393.

2,5-bis(tolyl)thiophene [Suzuki test reactions] (24). For all reactions, compound **23** (0.10 g, 0.32 mmol), 4-bromotoluene (0.11 g, 0.65 mmol), $NaHCO_3$(0.27g, 3.25 mmol), and 1 mol% $PdCl_2$(dppf) were used. Solvents were varied among THF, DMF, and toluene in a 5:1 by volume ratio with H_2O. Reactions were conducted at room temperature, 72 ^{0}C, or reflux either as one pot type reactions or compound **3** was added slowly to the reaction. 25 mL of H_2O and 50 mL of Et_2O were added after 6 hours. The organic layer was analyzed via gas chromatography and product identity determined solely by mass spectroscopy (GC/MS). No further identification or purification of the reactions was conducted. Table 3-1 summarizes the GC/MS results.

Poly({2,5-bis[2-(*N,N*-diethylamino)-1-oxapropyl]-1,4-phenylene}-*alt*-2,5-thienylene) (PPT-NEt$_2$).

General Procedure for Stille One Pot Synthesis. A 20 mL Schlenk flask with stir bar was charged with **DINEt** and 2,5-bis(trimethylstannyl)thiophene (**21**). The flask was evacuated and backfilled with Ar three times. 20 mL of anhydrous DMF, previously sparged with Ar for 30 min., was added to the reaction flask via syringe. The reaction mixture was stirred and heated to 50 ^{0}C, allowing all monomers to dissolve. $PdCl_2(PPh_3)_2$ was added in one portion and the reaction heated at 70 ^{0}C for a variable number of hours.

The DMF solution was concentrated to ~5 mL and precipitated into 150 mL MeOH. A dark red solid was collected on a medium porosity glass frit and subsequently extracted with MeOH for 24 hours, acetone for 24 hours, and then collected by extraction with chloroform (via Soxhlet extraction). The chloroform soluble fraction was collected by evaporation of the solvent and dried *in vacuo* at 50 ^{0}C overnight. ^{1}H NMR (300 MHz, $CDCl_3$) 7.63 (bm, 2 H), 7.34 (bm. 2 H), 4.24 (bm, 4 H), 3.04 (bm, 4 H), 2.69 (bm, 8 H), 1.11 (bm, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 149.53, 139.09, 126.49, 123.26, 113.26, 68.36, 52.09, 42.88, 12.01 ppm. UV-Vis (THF) λ_{max} = 460 nm, log ε_{max} = 4.26. PL (THF with 460 nm excitation) λ_{max} = 519 nm.

PPT-NEt$_2$(48)[25]. Reaction time of 48 hours. Reagents: **DINEt** (1.0895 g, 1.945 mmol), 2,5-bis(trimethylstannyl)thiophene (**21**) (0.7967 g, 1.945 mmol), and 32 mg of $PdCl_2(PPh_3)_2$ (0.03 mmol). 0.45 g of polymer was recovered (60% yield). Anal. calcd for $C_{22}H_{32}N_2O_2SI_{0.079}$: C, 66.33; H, 8.04; N, 7.03; I, 2.52. Found: C, 65.23; H, 7.84; N, 6.65; I, 2.50. GPC (THF vs. PS) $\overline{M}_n$ = 3,200 g mol^{-1}, *MP* = 4,300 g mol^{-1}, $\overline{M}_w$ = 5,200 g mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.70.

PPT-NEt$_2$(96)[26]. Reaction time of 96 hours. Reagents: **DINEt** (1.2568 g, 2.243 mmol), 2,5-bis(trimethylstannyl)thiophene (**21**) (0.9191 g, 2.243 mmol), and 37 mg of $PdCl_2(PPh_3)_2$ (0.04 mmol). 0.79 g of polymer was recovered (80% yield). Anal. calcd for $C_{22}H_{32}N_2O_2SI_{0.037}$: C, 67.13; H, 8.14; N, 7.12; I, 1.19. Found: C, 63.64; H, 8.03; N, 6.46; I, 1.20. GPC (THF vs. PS) $\overline{M}_n$ = 4,100 g mol^{-1}, *MP* = 5,800 g mol^{-1}, $\overline{M}_w$ = 6,900 g mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.68.

PPT-NEt$_2$(240)[27]. Reaction time of 240 hours. Reagents: **DINEt** (1.4298 g, 2.552 mmol), 2,5-bis(trimethylstannyl)thiophene (**21**) (1.0456 g, 2.552 mmol), and 35 mg of $PdCl_2(PPh_3)_2$ (0.05 mmol). 0.81 g of polymer was recovered (82% yield). Anal. calcd for $C_{22}H_{32}N_2O_2SI_{0.037}$: C, 67.13; H, 8.14; N, 7.12; I, 1.19. Found: C, 63.99; H, 7.99; N, 6.51; I, 1.22. GPC (THF vs. PS) $\overline{M}_n$ = 4,200 g mol^{-1}, *MP* = 5,400 g mol^{-1}, $\overline{M}_w$ = 7,200 g mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.71.

Procedure for Stille Dropwise Synthesis. PPT-NEt$_2$ (96-drop)[28]. A 20 mL Schlenk flask with stir bar was charged with **DINEt** (1.01 g, 1.80 mmol), 25 mg of $PdCl_2(PPh_3)_2$ (0.04 mmol), and 20 mL of anhydrous DMF, previously sparged with Ar for 30 min. The solution was warmed to 70 ^{0}C. 2,5-bis(trimethylstannyl)thiophene (**21**) (0.74 g, 1.80 mmol) was dissolved in 15 mL of DMF and added to a 20 mL addition funnel attached to the Schlenk flask. Compound **21** was added dropwise over the course of 4 hours. The reaction mixture was held at 70 ^{0}C for 96 hours. The DMF solution was concentrated to ~5 mL and precipitated into 150 mL MeOH. A dark red solid was collected on a medium porosity glass frit and subsequently extracted with MeOH for 24 hours, acetone for 24 hours, and then collected by extraction with chloroform (via Soxhlet extraction). The chloroform soluble fraction was collected by evaporation of the solvent and dried *in vacuo* at 50 ^{0}C overnight. 0.59 g of polymer was recovered (84% yield). ^{1}H NMR (300 MHz, $CDCl_3$) 7.63 (bm, 2 H), 7.34 (bm. 2 H), 4.24 (bm, 4 H), 3.04 (bm, 4 H), 2.69 (bm, 8 H), 1.11 (bm, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 149.53, 139.09, 126.49, 123.26, 113.26, 68.36, 52.09, 42.88, 12.01 ppm. Anal. calcd for $C_{22}H_{32}N_2O_2SI_{0.030}$: C, 67.38; H, 8.17; N, 7.15; I, 0.97. Found: C, 63.99; H, 8.02; N,

6.51; I, 0.98. GPC (THF vs. PS) $\overline{M}_n$ = 5,300 g mol^{-1}, *MP* = 6,900 g mol^{-1}, $\overline{M}_w$ = 9,000 g mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.70.

Procedure for Suzuki Dropwise Synthesis. PPT-NEt$_2$ (Suz)[29]. A 50 mL Schlenk flask with stir bar was charged with **DINEt** (0.8089 g, 1.44 mmol), 21 mg of $PdCl_2$(dppf) (0.03 mmol), and $NaHCO_3$ (1.53 g, 14.43 mmol). 10 mL DMF and 5 mL of H_2O previously sparged with Ar for 30 min. were then added. The solution was warmed to 70 ^{0}C. Compound **23** (0.4449 g, 1.44 mmol) was dissolved in 10 mL of DMF and added to a 20 mL addition funnel attached to the Schlenk flask. **23** was added dropwise over the course of 4 hours. The reaction mixture was held at 70 ^{0}C for 96 hours. The solution was concentrated to ~5 mL and precipitated into 150 mL MeOH. A light red solid was collected on a medium porosity glass frit and subsequently extracted with MeOH for 24 hours, acetone for 24 hours, and then collected by extraction with chloroform (via Soxhlet extraction). The chloroform soluble fraction was collected by evaporation of the solvent and dried *in vacuo* at 50 ^{0}C overnight. 0.28 g of polymer was recovered (50% yield). ^{1}H NMR (300 MHz, $CDCl_3$) 7.63 (bm, 2 H), 7.34 (bm. 2 H), 4.24 (bm, 4 H), 3.04 (bm, 4 H), 2.69 (bm, 8 H), 1.11 (bm, 12 H) ppm. Anal. calcd for $C_{22}H_{32}N_2O_2S$: C, 68.04; H, 8.23; N, 7.23. Found: C, 64.70; H, 7.98; N, 6.60; I, 0.09. UV-Vis (THF) λ_{max} = 452 nm, log ε_{max} = 3.98. GPC results showed a non-polymeric distribution and very low molecular weight species.

General Quaternization Procedure. Neutral alkoxy-amine containing polymers were stirred at room temperature with an excess of bromoethane in a minimal amount of THF under Ar with stirring. The partially quaternized amine polymers began to precipitate out of solution between 3-5 days at room temperature. The quaternized

polymer solution was precipitated into acetone, collected on a glass frit, washed thoroughly with acetone, and dried *in vacuo* at 50 ^{0}C overnight.

Poly{2,5-bis[2-(*N,N,N*-triethylammonium)-1-oxapropyl]-1,4-phenylene-*alt*-2,5-thienylene} dibromide (PPT-NEt$_3$+). ^{1}H NMR (300 MHz, D_2O) 7.22 (bm, 2 H), 6.90 (bm. 2 H), 3.96 (bm, 4 H), 3.12 (bm, 4 H), 2.70 (bm, 8 H), 0.55 (bm, 16.2 H) ppm. UV-Vis (H_2O) λ_{max} = 411 nm, log ε_{max} = 4.20. PL (H_2O with 411 nm excitation) λ_{max} = 494 nm.

PPT-NEt$_3$+(96)[30]. Anal. calcd for $C_{22}H_{32}N_2O_2SI_{0.037}$•2.0 C_2H_5Br: C, 51.09; H, 6.88; N, 4.58; Br, 26.20. Found: C, 49.87; H, 6.48; N, 3.18; Br, 24.18.

PPT-NEt$_3$+(96-drop)[31]. Anal. calcd for $C_{22}H_{32}N_2O_2SI_{0.030}$•2.0 C_2H_5Br: C, 51.16; H, 6.89; N, 4.59; Br, 26.24. Found: C, 49.73; H, 6.52; N, 3.29; Br, 23.62.

Chapter 4

General Procedure for Williamson Etherification of Hydroquinone. A suspension of powdered KOH in 100 mL of DMSO was added to a dry 250 mL three neck round bottom flask and stirred for 1 hour. Hydroquinone and the alkylbromide were added in one portion under a steady stream of Ar. The reactions were stirred and heated to 80 ^{0}C for 12 hours. Upon cooling, the reaction mixture was poured into 300 mL of H_2O. The aqueous mixture was extracted with hexane (3 x 100) and the combined organics washed with 1M NaOH (300 mL x 1, 150 mL x 1, 50 mL x 1), H_2O (300 mL x 1), and brine (300 mL x 1). After drying over $MgSO_4$, the solvent was removed by reduced pressure evaporation.

1,4-Bis(hexyloxy)benzene (32). Reagents: Hydroquinone (10.41 g, 94.6 mmol), hexylbromide (62.5 g, 378.5 mmol), and KOH (42.40 g, 757.0 mmol). Product was collected as a crude brownish solid and was recrystallized from ethanol giving 21.84 g of a white, crystalline material (83% yield). mp. 43-45 ^{0}C. ^{1}H NMR (300 MHz, $CDCl_3$) 6.82 (s, 4 H), 3.89 (t, 4 H), 1.75 (m, 4 H), 1.34-1.44 (bm, 12 H), 0.90 (t, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 153.12, 115.33, 68.62, 31.89, 29.56, 26.07, 22.70, 14.13 ppm.

1,4-Bis(nonyloxy)benzene (33). Reagents: Hydroquinone (3.99 g, 36.3 mmol), nonylbromide (22.53 g, 108.8 mmol), and KOH (16.24 g, 290.0 mmol). Product was collected as a crude brownish solid and was recrystallized from ethanol giving 10.33 g of a white, crystalline material (79% yield). mp. 56-58 ^{0}C. ^{1}H NMR (300 MHz, $CDCl_3$) 6.82 (s, 4 H), 3.89 (t, 4 H), 1.75 (m, 4 H), 1.34-1.44 (bm, 12 H), 0.90 (t, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 153.12, 115.33, 68.62, 31.89, 29.56, 29.42, 29.28, 26.07, 22.70, 14.13 ppm.

General procedure for the iodination of 1,4-dialkoxybenzenes. A 250 mL, 3 neck round bottom flask was charged with 1,4-dialkoxybenzene and a solvent system consisting of 90:7:3 HOAc/ H_2O/ H_2SO_4 by volume. $CHCl_3$ was added until the 1,4-dialkoxybenzene dissolved. I_2 and KIO_4 were added and the reaction heated to 70 ^{0}C overnight. The reaction was cooled, poured into 500 mL H_2O, and extracted with chloroform (3 x 150). The combined organics were dried over $MgSO_4$ and the solvent evaporated. Purification was accomplished by recrystallization or column chromatography, depending on the compound.

1,4-Bis(hexyloxy)-2,5-diiodobenzene (34). Reagents: 1,4-Bis(hexyloxy)benzene (13.43 g, 48.3 mmol), I_2 (15.07 g, 58.0 mmol), and KIO_4 (13.33 g,

58.0 mmol). Product was collected as a crude red/brown solid and purified by recrystallization from ethanol yielding 20.20 g of a white, crystalline solid (79% yield). mp. 52-53 ^{0}C. ^{1}H NMR (300 MHz, $CDCl_3$) 7.12 (s, 2 H), 3.92 (t, 4 H), 1.80 (m, 4 H), 1.35-1.50 (bm, 12 H), 0.91 (t, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 152.89, 122.87, 86.34, 70.42, 31.47, 29.14, 25.72, 22.59, 14.02 ppm. Anal. Calcd for $C_{18}H_{28}O_2I_2$: C, 40.75 ; H, 5.32. Found: C, 40.68; H, 5.31; N, 4.90. FAB-HRMS $(M)^+$ calculated for $C_{18}H_{28}O_2I_2$: 530.0179, Found 530.0178.

1,4-Bis(nonyloxy)-2,5-diiodobenzene (35). Reagents: 1,4-Bis(nonyloxy)benzene (9.14 g, 25.2 mmol), I_2 (7.86 g, 30.3 mmol), and KIO_4 (6.95 g, 30.3 mmol). Product was collected as a crude red/brown solid and purified by recrystallization from ethanol yielding 13.13 g of a white, crystalline solid (85% yield). mp. 52-53 ^{0}C. ^{1}H NMR (300 MHz, $CDCl_3$) 7.12 (s, 2 H), 3.93 (t, 4 H), 1.81 (m, 4 H), 1.29-1.50 (bm, 24 H), 0.89 (t, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 152.80, 122.73, 86.28, 70.33, 31.89, 29.52, 29.27, 29.14, 26.04, 22.70, 14.15 ppm. Anal. Calcd for $C_{24}H_{40}O_2I_2$: C, 46.90 ; H, 6.56. Found: C, 46.75; H, 6.83. FAB-HRMS $(M)^+$ calculated for $C_{24}H_{40}O_2I_2$: 614.1118, Found 614.1116.

General Procedure for the Sonogashira coupling of trimethylsilylacetylene to diiodobenzenes. The appropriate diiodobenzene, $PdCl_2(PPh_3)_2$, and CuI were added to a dry 150 mL side-arm flask under argon. Dry Et_3N was added to the reaction via cannula (~75 mL). The reaction mixture was stirred until reagents have dissolved and 3.0 equivalents of trimethylsilylacetylene are added in one portion. The reaction was heated to 70 ^{0}C and stirred overnight. After cooling, the reaction was filtered to remove

ammonium salts and passed through a silica gel plug using an appropriate solvent. After removal of solvent, the solids were recyrstallized twice from methanol or ethanol.

1,4-Bis((trimethysilyl)ethynyl)-benzene (38). Reagents: 1,4-diidobenzene (3.00 g, 9.1 mmol), trimethylsilylacetylene (2.00 g, 20.0 mmol), $PdCl_2(PPh_3)_2$ (0.26 g, 0.4 mmol), and CuI (0.03 g, 0.2 mmol). Product was collected as a crude black solid and purified by column chromatography on silica gel (1:1 hexanes/CH_2Cl_2) followed by recrystallization from MeOH giving white crystals (2.21 g, 90% yield). mp. 119-122 ^{0}C. ^{1}H NMR (300 MHz, $CDCl_3$) 7.40 (s, 4 H), 0.25 (s, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 131.74, 123.14, 104.55, 96.29, -0.03 ppm. Anal. Calcd for $C_{16}H_{22}Si_2$: C, 71.08 ; H, 8.06. Found: C, 70.45; H, 8.06. FAB-HRMS $(M)^+$ calculated for $C_{16}H_{22}Si_2$: 270.1260, Found 270.1255.

1,4-Bis((trimethysilyl)ethynyl)-2,5-bis(hexyloxy)benzene (36). Reagents: 1,4-bis(hexyloxy)-2,5-diiodobenzene (3.06 g, 5.8 mmol), trimethylsilylacetylene (1.73 g, 17.3 mmol), $PdCl_2(PPh_3)_2$ (0.41 g, 0.6 mmol), and CuI (0.11 g, 0.6 mmol). Product was collected as a crude black solid and purified by column chromatography on silica gel (1:1 hexanes/CH_2Cl_2) followed by recrystallization from MeOH giving faint yellow crystals (2.18 g, 80% yield). ^{1}H NMR (300 MHz, $CDCl_3$) 6.89 (s, 2 H), 3.94 (t, 4 H), 1.78 (m, 4 H), 1.50 (m, 4 H), 1.34 (m, 8 H), 0.90 (t, 6 H), 0.25 (s, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 154.03, 117.33, 114.04, 101.09, 100.02, 69.52, 31.61, 29.32, 25.70, 22.63, 14.05, -0.03 ppm. Anal. Calcd for $C_{28}H_{46}O_2Si_2$: C, 71.44 ; H, 9.86. Found: C, 70.75; H, 10.09. FAB-HRMS $(M)^+$ calculated for $C_{28}H_{46}O_2Si_2$: 470.3036, Found 470.3051.

1,4-Bis((trimethysilyl)ethynyl)-2,5-bis(nonyloxy)benzene (37). Reagents: 1,4-bis(nonyloxy)-2,5-diiodobenzene (2.55 g, 4.2 mmol), trimethylsilylacetylene (1.22 g,

12.5 mmol), $PdCl_2(PPh_3)_2$ (0.06 g, 0.1 mmol), and CuI (0.016 g, 0.1 mmol). Product was collected as a crude red solid and purified by column chromatography on silica gel (toluene) followed by recrystallization from ethanol giving faint yellow crystals (1.71 g, 74% yield). ^{1}H NMR (300 MHz, $CDCl_3$) 6.89 (s, 2 H), 3.94 (t, 4 H), 1.78 (m, 4 H), 1.50-1.27 (m, 24 H), 0.88 (t, 6 H), 0.25 (s, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 153.96, 117.11, 113.87, 101.02, 100.05, 69.39, 31.91, 29.61, 29.51, 29.45, 29.32, 26.03, 22.68, 14.13, -0.03 ppm. Anal. Calcd for $C_{34}H_{58}O_2Si_2$: C, 73.59 ; H, 10.54. Found: C, 73.76; H, 11.17. FAB-HRMS $(M)^+$ calculated for $C_{34}H_{58}O_2Si_2$: 554.3975, Found 554.3978.

General Procedure for the removal of trimethylsilyl groups. The appropriate 1,4-bis((trimethysilyl)ethynyl)-2,5-dialkoxybenzene was dissolved in THF and excess tetrabutylammonium fluoride was added with stirring. The solutions were stirred for two hours during which time a very dark black coloration of the solution occurred. The reaction was poured into 300 mL of H_2O and extracted three times with hexanes. The combined organics were washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the solid products were recrystallized in hexane. 1,4-diethynylbenzene was further purified via vacuum sublimation.

1,4-diethynylbenzene (41). Reagents: 1,4-bis((trimethysilyl)ethynyl)-benzene (3.02 g, 11.2 mmol). Solid product was recrystallized from MeOH and vacuum sublimed to produce 1.24 g of a white solid in 88% yield. ^{1}H NMR (300 MHz, $CDCl_3$) 7.42 (s, 4 H), 3.15 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 131.98, 122.57, 83.01, 79.03 ppm. Anal. Calcd for $C_{10}H_6$: C, 95.20 ; H, 4.80. Found: C, 95.60; H, 4.60. FAB-HRMS $(M)^+$ calculated for $C_{10}H_6$: 126.0470, Found 126.0475.

1,4-diethynyl-2,5-bis(hexyloxy)benzene (39). Reagents: 1,4-bis((trimethysilyl)ethynyl)-2,5-bis(hexyloxy)benzene (1.91 g, 4.1 mmol). Solvent was removed to give a yellow crude material which was passed through a silica gel column (1:1 hexanes/CH_2Cl_2) and crystallized from hexane resulting in collection of 1.25 g of a light yellow material (94 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) 6.95 (s, 2 H), 3.97 (t, 4 H), 3.34 (s, 2H), 1.80 (m, 4 H), 1.34-1.47 (m, 12 H), 0.90 (t, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 154.03, 117.33, 114.04, 101.09, 100.02, 69.52, 31.61, 29.32, 25.70, 22.63, 14.05 ppm. Anal. Calcd for $C_{22}H_{30}O_2$: C, 80.93 ; H, 9.27. Found: C, 81.20; H, 9.15. FAB-HRMS $(M)^+$ calculated for $C_{22}H_{30}O_2$: 326.2246, Found 326.2240.

1,4-diethynyl-2,5-bis(nonyloxy)benzene (40). Reagents: 1,4-bis((trimethysilyl)ethynyl)-2,5-bis(nonyloxy)benzene (1.52 g, 2.7 mmol). After extractions, solvent was removed to give a crude yellow material which was crystallized from hexane to give 1.06 g of a light yellow material (95 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) 6.95 (s, 2 H), 3.97 (t, 4 H), 3.33 (s, 2 H), 1.80 (m, 4 H), 1.20-1.60 (m, 24 H), 0.88 (t, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 153.97, 117.76, 113.27, 82.36, 79.77, 69.66, 31.86, 29.49, 29.30, 29.21, 29.11, 25.87, 22.65, 14.07 ppm. Anal. Calcd for $C_{28}H_{42}O_2$: C, 81.89; H, 10.32. Found: C, 82.02; H, 10.68. FAB-HRMS $(M)^+$ calculated for $C_{28}H_{42}O_2$: 410.3185, Found 410.3183.

Compounds 43-45. See reference 54c for complete synthetic details.

2,5-Bis(6-bromohexyl)-1,4-diiodobenzene (46). A 250 mL, 3 neck round bottom flask was charged with compound **45** (2.11 g, 5.22 mmol) and a solvent system consisting of 90:7:3 HOAc/ H_2O/ H_2SO_4 by volume. $CHCl_3$ was added until compound **45** was dissolved. I_2 (1.63 g, 6.27 mmol) and KIO_4 (1.44 g, 6.27 mmol) were added and

the reaction heated to 70 ^{0}C overnight. The reaction was cooled, poured into 500 mL H_2O, and extracted with chloroform (3 x 150). The combined organics were dried over $MgSO_4$ and the solvent evaporated. Purification of the crude brown solid was accomplished via recrystallization from MeOH and a minimal amount of acetone (2.20 g, 65% yield). mp 74-75 ^{0}C. ^{1}H NMR (300 MHz, $CDCl_3$) 7.59 (s, 2 H), 3.42 (t, 4 H), 2.61 (t, 4 H), 1.89 (m, 4 H), 1.42-1.57 (m, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 144.60, 139.32, 100.31, 39.64, 33.93, 32.67, 29.97, 28.38, 27.92 ppm. Anal. Calcd for $C_{18}H_{26}Br_2I_2$: C, 33.04 ; H, 4.01; I, 38.82. Found: C, 33.08; H, 3.98; I, 38.98. FAB-HRMS $(M)^+$ calculated for $C_{18}H_{26}Br_2I_2$: 653.8491, Found 653.8493.

2,5-Bis(6-phenoxyhexyl)-1,4-diiodobenzene (50). A solution of compound **46** (5.08 g, 7.77 mmol) in dry toluene (25 mL) was added slowly to a stirred solution of phenol (2.82 g, 31.06 mmol), sodium *t*-butoxide (2.69 g, 27.18 mmol), and potassium iodide (catalytic) in anhydrous DMF (75 mL). The mixture was stirred and refluxed for 16 hours. Water was added (100 mL) and the organic layer separated off with the aqueous layer being extracted with benzene (3 x 100mL). The combined organic layers were washed with 1M NaOH (3 x 100mL), water (2 x 100 mL), and brine (1 x 100 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* and the obtained crude product was recrystallized from hexane (3.91 g, 74% yield). mp. 88-89 ^{0}C. ^{1}H NMR (300 MHz, $CDCl_3$) 7.59 (s, 2 H), 7.26 (m, 4 H), 6.91 (m, 6 H), 3.96 (t, 4 H), 2.61 (t, 4 H), 1.81 (m, 4 H), 1.50 (m, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 158.99, 144.65, 139.28, 129.37, 120.44, 114.43, 100.29, 67.69, 39.71, 30.11, 29.20, 29.03, 25.86 ppm. Anal. Calcd for $C_{30}H_{36}O_2I_2$: C, 52.78 ; H, 5.32. Found: C, 52.48; H, 5.69. FAB-HRMS $(M)^+$ calculated for $C_{30}H_{36}O_2I_2$: 682.0805, Found 682.0766.

General Sonogashira Polymerization Procedure for Poly(*p*-phenyleneethynylene)'s (PPE-NEt/R). The appropriate 1,4-diethynyl compound (1.02 equivalents), **DINEt**, $Pd(PPh_3)_4$ (5 mol%), and CuI (5 mol%) are placed in a dry 50 mL Schlenk flask and evacuated and backfilled with Ar three times. A 2:1 by volume solution of thoroughly sparged toluene and diisopropylamine solvent system was added to the reaction via syringe in an amount making the reaction 0.05 M in **DINEt**. The reaction was heated to 70 ^{0}C for 24 hours. In the case of endcapping experiments, the appropriate amount of iodobenzene was added to the reaction via syringe immediately after the solvent addition prior to heating. A second aliquot of iodobenzene was added after 24 hours and allowed to react for 2 hours before cooling to ensure maximum endcapping. The polymerizations were cooled and precipitated into acetone. The polymers were extracted with hot ethanol, acetone, and acetonitrile after collection. See Chapter 4 text for discussion on polymer drying methodologies and solubilities.

Polymer PPE-NEt_2/H[51] . Reagents: **DINEt** (0.4532 g, 0.809 mmol), 1,4-diethynylbenzene (**41**) (0.1040 g, 0.825mmol), CuI (7.7 mg, 0.040 mmol)and 47.7 mg of $Pd(PPh_3)_4$ (0.040 mmol). 0.340 g of polymer was recovered (98% yield). Anal. calcd for $C_{28}H_{34}N_2O_2$: C, 78.10; H, 7.96; N, 6.51. Found: C, 74.30; H, 7.08; N, 6.32. The polymer precipitated during the coarse of the reaction and was insoluble after collection and drying.

Polymer PPE-NEt_2/OC6[52] . Reagents: **DINEt** (0.8959 g, 1.600 mmol), 1,4-diethynyl-2,5-bis(hexyloxy)benzene (**39**) (0.5321 g, 1.631 mmol), CuI (15.3 mg, 0.080 mmol) and 92.4 mg of $Pd(PPh_3)_4$ (0.080 mmol). 0.998 g of polymer was recovered (99% yield). Anal. calcd for $C_{40}H_{58}N_2O_4$: C, 76.15; H, 9.27; N, 4.44. Found: C, 72.10; H,

7.89; N, 4.01. A small portion of the polymer precipitated during the reaction. 100 mg of soluble material could be extracted with an excess of boiling chloroform after precipitation and drying.

Polymer PPE-NEt$_2$/OC9 (High)[53]. Reagents: **DINEt** (0.3738 g, 0.667 mmol), 1,4-diethynyl-2,5-bis(nonylloxy)benzene (**40**) (0.2792 g, 0.6805 mmol), CuI (6.2 mg, 0.033 mmol)and 38.4 mg of $Pd(PPh_3)_4$ (0.033 mmol). 0.472 g of polymer was recovered (99% yield). Anal. calcd for $C_{46}H_{70}N_2O_4$: C, 77.27; H, 9.87; N, 3.92. Found: C, 76.11; H, 9.79; N, 3.47; I, 0.55. The polymer formed a "gel" during the reaction, which was dissolved with excess chloroform. After precipitation, washing, and drying, the polymer was completely insoluble in any common organic boiling solvent.

Polymer PPE-NEt$_2$/OC9 (20)[54]. Reagents: **DINEt** (0.3685 g, 0.658 mmol), 1,4-diethynyl-2,5-bis(nonylloxy)benzene (**40**) (0.2753 g, 0.671 mmol), iodobenzene (7.2 mg, 0.035 mmol), CuI (6.3 mg, 0.033 mmol) and 38.0 mg of $Pd(PPh_3)_4$ (0.033 mmol). 0.44 g of polymer was recovered (99% yield). Anal. calcd for $C_{46}H_{70}N_2O_4$: C, 77.27; H, 9.87; N, 3.92. Found: C, 75.80; H, 9.58; N, 3.45. The polymer remained soluble during the reaction and upon precipitation and complete drying a small amount of material was soluble in chloroform. The experiment was conducted a second time using the conditions above and the polymer was collected via gravity filtration through coarse filter paper and only air dried. The "solvated" polymer displayed much greater solubility allowing for more complete analyses and conversion to the cationic polyelectrolyte. ^{1}H NMR (300 MHz, $CDCl_3$) 7.04 (bs, 2 H), 7.02 (bs. 2 H), 4.12 (bm, 4 H), 4.03 (bm, 4 H), 2.98 (bs, 4 H), 2.68 (bm, 8 H), 1.87 (bm, 4 H), 1.52 (bm, 4 H), 1.26 (bm, 20 H), 1.06 (bm, 12 H), 0.88 (bt, 6 H); Endgroup 7.55 (m, 0.17 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$) 153.44,

117.09, 77.93, 69.59, 68.24, 51.58, 47.94, 31.88, 29.69, 29.61, 29.41, 29.30, 25.93, 22.67, 14.11, 12.16 ppm . Anal. calcd for $C_{46}H_{70}N_2O_4$: C, 77.27; H, 9.87; N, 3.92. Found: C, 75.66; H, 9.64; N, 3.41; I, 0.37. UV-Vis ($CHCl_3$) λ_{max} = 442 nm, log ε_{max} = 4.63. UV-Vis (1M HCl in EtOH, **PPE-NEt$_2$H+/OC9(20)[55]**) λ_{max} = 408 nm, log ε_{max} = 5.04. PL ($CHCl_3$) λ_{max} = 502 nm; Quantum Yield = 0.001. PL (1M HCl in EtOH, **PPE-NEt$_2$H+/OC9(20)[55]**) λ_{max} = 464 nm; Quantum Yield = 0.86. $\overline{M}_n$ (via ^{1}H NMR) = 16,500 g/mol.

Polymer PPE-NEt$_3$+/OC9(20)[56]. PPE-NEt$_2$/OC9(20)[54] (0.173 g, 0.24 mmol) was dissolved in 50 ml of $CHCl_3$ and an excess of bromoethane was added (10 mL). The reaction was heated to 50^{0}C and stirred for 3 days. Each day ~10 mL of acetonitrile was added to ensure that the polyelectrolyte being formed remained in solution. Over the coarse of the reaction, a swollen orange material did precipitate from the reaction. The reaction was cooled, concentrated, and added to 200 mL of THF. 200 mg of an orange solid was recovered (88% yield). The material was poorly soluble in ethanol and insoluble in water, chloroform, and THF. The portion of material soluble in ethanol displayed optical absorbances similar to that of **PPE-NEt$_2$H+/OC9(20)[55]**. Anal. calcd for $C_{50}H_{80}N_2O_4Br_2$: C, 64.37; H, 8.64; N, 3.00; Br. 17.13. Found: C, 66.06; H, 8.92; N, 3.03; Br, 12.58.

CHAPTER 7
REFERENCES

1. Staudinger, H. *Die Hochmolecularen:* Springer-Verlag: Berlin, 1932.

2. Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 11.

3. Lieser, G.; Wegner, F.; Müller, W.; Enkelmann, V.; Meyer, W.J. *Makromol. Chem. Rap. Commun.* **1980**, *1*, 627.

4. Frost, A.A.; Musulin, B. *J. Chem. Phys.* **1953**, *21*, 572.

5. Jahn, H.A.; Teller, E. *Proc. Roy. Soc.* **1937**, *A161*, 220.

6. Peierls, R.E. In *Quantum Theory of Solids*; Oxford Univ. Press: London 1955; p 108.

7. Williams, J.M. In *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 235.

8. (a) Shirakawa, H.; Louis, E.J.; MacDiarmid, A.G.; Chiang, C.K.; Heeger, A.J. *J. Chem. Soc., Chem. Commun.* **1977**, 578. (b) Chiang, C.K.; Druy, M.A.; Gau, S.C.; Heeger, A.J.; Louis, E.J.; MacDiarmid, A.G.; Park, Y.W.; Shirakawa, H. *J. Am. Chem. Soc.* **1978**, *100*, 1013.

9. Su, W.P.; Schrieffer, J.R.; Heeger, A.J. *J. Phys. Rev. Lett.*, **1979**, *42*, 1698.

10. Maarman, H.; Theophilou, N. *Synth. Met.*, **1987**, *22*, 1.

11. *Handbook of Conducting Polymers*; Skotheim, T.A.; Elsenbaumer, R.L.; Reynolds, J.R., Eds.; Marcel Dekker: New York, 1998.

12. Pope, M.; Kallmann, H.; Magnante, P. *J. Chem. Phys.* **1963**, *38*, 229.

13. Burroughes, J.H.; Bradley, D.D.C.; Brown, A.R.; Marks, R.N.; Mackay, K.; Friend, R.H.; Burn, P.L.; Holmes, A.B. *Nature* **1990**, *347*, 539.

14. (a) Su, W.-P.; Schrieffer, J.R.; Heeger, A.J. *Phys. Rev.Lett.*. **1979**, *42*, 1698. (b) Su, W.-P.; Schrieffer, J.R.; Heeger, A.J. *Phys. Rev. B.* **1980**, *22*, 2099. (c) Rice, M.J. *Phys. Lett. A* **1979**, *71*, 152.

15. (a) Shuai, Z.; Brédas, J.L.; Su, W.P. *Chem. Phys. Lett.* **1994**, *228*, 301. (b) Beljonne, D.; Shuai, Z.; Friend, R.H.; Brédas, J.L. *J. Chem. Phys.* **1995**, *102*, 2042.

16. Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36.

17. Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phus.* **1991**, *30*, L1941.

18. Parker, I.D.; Pei, Q.; Marrocco, M. *Appl. Phys. Lett.* **1994**, *65*, 1272.

19. Grüner, J.F.; Friend, R.H.; Scherf, U.; Huber, J.; Holmes, A.B. *Adv. Mater.* **1994**, *6*, 748.

20. (a) Burn, P.L.; Holmes, A.B.; Kraft, A.; Bradley, D.D.C.; Brown, A.R.; Friend, R.H. *J. Chem. Soc., Chem. Commun.* **1992,** 32. (b) Burn, P.L.; Holmes, A.B.; Kraft, A.; Bradley, D.D.C.; Brown, A.R.; Friend, R.H.; Gymer, R.W. *Nature* **1992**, *356*, 47. (c) Braun, D.; Staring, E.G.J.; Demandt, R.C.J.E.; Rikken, L.J.; Kessener, Y.A.R.R.; Venhuizen, A.H.J. *Synth. Met.* **1994**, *6*, 934. (d) Staring, E.G.J.; Demandt, R.C.E.; Braun, D.; Rikken, G.L.J.; Kessener, Y.A.R.R.; Venhuzen, T.H.J.; Wynberg, H.; ten Hoeve, W.; Spoelstra, K.J. *Adv. Mater.* **1994**, *6*, 934.

21. (a) Braun, D.; Heeger, A.J. *Appl. Phys. Lett.* **1991**, *58*, 1982. (b) Braun, D.; Heeger, A.J. *Appl. Phys. Lett.* **1991**, *59*, 878.

22. (a) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1991**, *30*, L1938. (b) Braun, D.; Sutafson, G.; McBranch, D.; Heeger, A.J. *J. Appl. Phys.* **1992**, *72*, 564. (c) Greenham, N. C.; Brown, A.R. Bradley, D.D.C.; Friend, R.H. *Synth. Met.* **1993**, *55-57*, 4134.

23. Yamamura,M; Moritani, I.; Murahashi, S. *J. Organomet. Chem.* **1975**, *91*, C39.

24. (a) Negishi, E.; Baba, S. *J. Chem. Soc., Chem. Commun.* **1976**, 596. (b) Baba, S.; Negishi, E. *J. Am. Chem. Soc.* **1976**, *98*, 6729.

25. Negishi, E.; King, A.O.; Okukado, N. *J. Org. Chem.* **1977**, *42*, 1821.

26. Negishi, E.; Van Horn, D.E. *J. Am. Chem. Soc.* **1977**, *99*, 3168.

27. Murahashi, S;. Yamamura, M.; Yanagisawa, K.; Mita, N.; Kondo, K. *J. Org. Chem.* **1979**, *44*, 2408.

28. (a) Milstein, D.; Stille, J.K. *J. Am. Chem. Soc.* **1979**, *101*, 4992. (b) Scott, W.J.; Crisp, G.T.; Stille, J.K. *J. Am. Chem. Soc.* **1984**, *106*, 4630. (c) Scott, W.J.; Stille, J.K. *J. Am. Chem. Soc.* **1986**, *108*, 3033. (d) Echavarren, A.M.; Stille, J.K. *J. Am. Chem. Soc.* **1987**, *109*, 5478. (e) Review: Stille, B.J. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508.

29. (a) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918. (b) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1989**, *54*, 268. (c) Hatanaka, Y.; Matsui, K.; Hiyama, T. *Tetrahedron Lett.*. **1989**, *30*, 2403. (d) Hatanaka, Y.; Hiyama, T. *J. Am. Chem Soc.*. **1990**, *112*, 7793. (e) Review: Hatanaka, Y.; Hiyama, T. *Synlett* **1991**, 845.

30. (a) Suzuki, A. *Acc. Chem. Res.* **1982**, *15*, 178. (b) Suzuki, A. *Pure Appl. Chem.* **1985**, *57*, 1749. (c) Miyaura, N.; Suzuki, A. *J. Synth. Org. Chem. Jpn.* **1988**, *46*, 848. (d) Miyaura, N.; Suzuki, A. *J. Synth. Org. Chem. Jpn.* **1993**, *51*, 1043. (e) Suzuki, A. *Pure Appl. Chem.* **1991**, *63*, 419. (f) Suzuki, A. *Pure Appl. Chem.* **1994**, *66*, 213.

31. (a) Heck, R.F. *J. Am. Chem. Soc.* **1968**, *90*, 5518. (b) Recent Review: Crisp, G.T. *Chem. Soc. Rev.* **1998**, *27*, 427.

32. Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

33. General Reviews: (a) Kochi, J.K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978. (b) Heck, R.F. *Palladium Reagents in Organic Syntheses*; Academic: New York, 1985. (c) Hartley, F.R.; Patai, S. *The Chemistry of Metal-Carbon Bond*; Wiley: New York, 1985; Vol. 3. (d) McQuillin, F.J.; Parker, D.G.; Stephenson, G.R. *Transition Metal Organometallics for Organic Synthesis*; Cambridge University Press: Cambridge, 1991. (e) Tamao, K. *Comprehensive Organic Synthesis;* Trost, B.M., Fleming, I., Pattenden, G., Eds.; Pergammon: New York, 1991; Vol. 3, p 435. (f) Hegedus, L.S. *Organometallics in Organic Synthesis*; Schlosser, M., Ed.; Willey: New York, 1994; p 383.

34. (a) Förster, S.; Schmidt, M. *Adv. Poly. Sci.* **1995**, *120*, 51. (b) Schmitz, K.S. *Macroions in Solution and Colloid Suspension*; VCH Publishers: New York, 1993. (c) MacCallum, J.R.; Vincent, C.A.. *Polymer Electrolyte Reviews*; Elsevier: London: 1987.

35. Steven, M.J.; Kremer, K. *J. Chem. Phys.* **1995**, *103*, 1669.

36. Kesting, R.E. *Synthetic Polymeric Membranes*, 2nd. Ed.; Wiley: New York, 1985.

37. (a) Ried, W.; Freitag, D. *Naturwiss.* **1966**, *53*, 305. (b) Dineen, J.M.; Volpe, A.A. *Am. Chem. Soc., Poly. Div., Polym. Prepr.* **1978**, *19*, 34. (c) Krigbaum, W.R.; Krause, K.J. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 3151. (d) Dineen, J.M.; Howell, E.E.; Volpe, A.A. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *23*, 1259. (e) Ballard, D.G.H.; Courtis, A.; Shirley, I.M.; Taylor, S.C. *J. Chem. Soc., Chem. Commun.* **1983**, 954. (f) Mukai, K.; Teshirogi, T.; Kuramoto, N.; Kitamura, T. *J. Polym. Sci., Poly. Chem. Ed.* **1985**, *23*, 1259. (g) Brédas, J.L. *J.Chem. Phys.* **1985**, *82*, 3808.

38. (a) Noren, G.K.; Stille, J.K. *Macromol. Rev.* **1971**, *5*, 385. (b) Gale, D.M. *J. Appl. Polym. Sci.* **1978**, *22*, 1971. (c) Baughman, R.H.; Brédas, J.L.; Chance, R.R.; Elsenbaumer, R.I.; Schacklette, L.W. *Chem. Rev.* **1982**, *82*, 209. (d) Jones, M.B.; Kovacic, P. In *Comprehensive Polymer Science*; Aggarwal, S.L., Russo, S., Eds.; Pergammon: Oxford, 1989; Suppl. 1, p. 318.

39. (a) Burroughes, J.H.; Bradley, D.D.C.; Brown, A.R.; Marks, R.N.; Mackay, K.; Friend, R.H.; Burn, P.L.; Holmes, A.B. *Nature* **1990**, *347*, 539. (b) Yamamoto, T. *Prog. Poly. Sci.* **1992**, *17*, 1153. (c) Grem, G.; Leditzky, G., Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36. (d) Stephens, E.B.; Tour, J.M. *Macromolecules* **1993**, *26*, 2420.

40. Yamamoto, K.; Nishide, H.; Tsuchida, E. *Polym. Bull.* **1987**, 17, *163.*

41. Stille, J.K.; Gillimas, Y. *Macromolecules* **1971**, *4*, 515.

42. (a) Kovacic, P.; Wu, C. *J. Poly. Sci.* **1960**, *47*, 448. (b) Brown, C.E.; Kovacic, P.; Wilkie, C.A.; Kinsinger, J.A.; Hein, R.E.; Yaniger, S.I.; Cody, R.B. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 255.

43. Ballard, D.G.H.; Courtis, A.; Shirley, I.M.; Taylor, S.C. *Macromolecules* **1988**, *21*, 294.

44. Gin, D.L.; Conticello, V.P.; Grubbs, R.H. *J. Am. Chem. Soc.* **1992**, *114*, 3167.

45. John, J.A.; Tour, J.M. *J. Am. Chem. Soc.* **1994**, *116,* 5011.

46. Yamamoto, T.; Hayashi, Y.; Yamamoto, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2091.

47. (a) Wang, Y.; Quirk, R.P. *Macromolecules* **1995** *28*, 3495. (b) Kaeriyama, K.; Mehta, M.A.; Masuda, H. *Synth. Met.* **1995**, 507.

48. Percec, V.; Bae, J.-Y.; Zhao, M.; Hill, D. H. *Macromolecules* **1995**, *28*, 6726.

49. Percec, V.; Okita, S.; Weiss, R. *Macromolecules* **1992**, *25*, 1816.

50. Rehahn, M.; Schlüter, A.-D.; Wegner, G.; Feast, W.J. *Polymer* **1989**, *30*, 1054.

51. Rehahn, M.; Schlüter, A.-D.; Wegner, G.; Feast, W.J. *Polymer* **1989**, *30*, 1060.

52. Rehahn, M.; Schlüter, A.-D.; Wegner, G.; Feast, W.J. *Makromol. Chem* **1990**, *191*, 1991.

53. (a) Lee, C.C.; Chu, S.-G.; Berry, G.C. *J. Polym. Sci.: Polym. Phys. Ed.* **1983**, *21*, 1573. (b) Metzger Cotts, P.; Berry, G.C. *J. Polym. Sci.: Polym. Phys. Ed.* **1983**, *21*, 1255.

54. (a) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411. (b) Rau, I.U.; Rehahn, M. *Makromol. Chem. Phys.* **1993**, *194*, 2225. (c) Rau, I.U.; Rehahn, M. *Polymer* **1993**, *34*, 2889. (c) Rau, I.U.; Rehahn, M. *Acta Polymerica* **1994**, *45*, 3.

55. Rulkens, R.; Schulze, M.; Wegner, G. *Macromol. Rapid Commun.* **1994**, *15*, 669.

56. (a) Child, A.D.; Reynolds, J.R. *Macromolecules* **1994**, *27*, 1975. (b) Kim, S.; Jackiw, J.; Robinson, E.; Schanze, K. S.; Reynolds, J. R.; Baur, J.; Rubner, M. F.; Boils, D. *Macromolecules* **1998**, *31*, 964.

57. Brodowski, G.; Horvath, A.; Ballauff, M.; Rehahn, M. *Macromolecules* **1996**, *29*, 6962.

58. (a) Balanda, P.B.; Ph.D. Dissertation, University of Florida 1997. (b) Balanda, P.B.; Ramey, M.B.; Reynolds, J.R. *Macromolecules* **1999**, *32*, 3970.

59. Baur, J.; Kim, S.; Balanda, P. B.; Reynolds, J. R.; Rubner, M. F. *Adv. Mater.*,**1998**, *10*, 1452.

60. Chang, S.C.; Bharathan, J.; Helgeson, R.; Wudl, F.; Yang, Y.; Ramey, M.B.; Reynolds, J.R. *Appl. Phys. Lett.*, **1998**, *73*, 2561.

61. Hong, L.; Powell, D. R.; Hayashi, R. K.; West, R. *Macromolecules* **1998**, *31*, 52.

62. Peng, Z.; Gharavi, A. R.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 4622.

63. Coutts, I. G. C.; Goldschmid, H. R.; Musgrave, O. C. *J. Chem. Soc.(C)* **1970**, 488.

64. Rehahn, M.; Schluter, A.-D.; Wegner, G. *Makromol. Chem.* **1990**, *191*, 1991.

65. Harrison, B.S.; Ramey, M.B.; Reynolds, J.R.; Schanze, K.S. *J. Am. Chem. Soc.* **2000**, *122*, 8561.

66. Moreno-Mañas, M.; Pérez, M.; Pleixats, R. *J. Org. Chem.* **1996**, *61*, 2346.

67. Kowitz, C.; Wegner, G. *Tetrahedron* **1997**, *53*, 15553.

68. Hayahi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.

69. Steffen, W.L.; Palenik, G. J. *J. Inorg. Chem.* **1976**, *5*, 2432.

70. Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995**, *60*, 7508.

71. Power, K.L.; Vries, T.R.; Havinga, E.E.; Meijer, E.W.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1988**, 1432.

72. Czerwinski, W.; Nucker, N.; Fink, J. *Synth. Met.* **1988**, *25*, 71.

73. (a) Danieli, R.; Ostoja, R.; Tiecco, M.; Zamboni, R.; Taliani, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1473. (b) Mitsuhara, T.; Tanaka, S.; Kaeriyama, K. *Makromol. Chem.* **1988**, *189*, 1755. (c) Tanak, S.; Kaeriyama, K.; Hiraide, T. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 743. (d) Ruiz, J.P.; Child, A.D.; Nayak, K.; Marynick, D.S.; Reynolds, J.R. *Synth. Met.* **1991**, *41*, 783. (e) Reynolds, J.R.; Ruiz, J.P.; Child, A.D.; Nayak, K.; Marynick, D.S. *Macromolecules.* **1991**, *24*, 783.

74. Pelter, A.; Maud, J.M.; Jenkins, I.; Sadeka, C.; Coles, G. *Tetrahedron Lett.*, **1989**, *30*, 3461.

75. Bao, Z.; Waikin, C.; Yu, L. *Chem. Mater.* **1993**, *51*, 2.

76. Bradley, D.D. *Chem. Brit.* **1991**, 719.

77. Bao, Z.; Waikin, C.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 12426.

78. Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585.

79. Echavarren, A.M.; Stille, J.K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.

80. (a) Segelstein, B.E.; Butler, T.W.; Chenard, B.L. *J. Org. Chem.* **1995**, *60*, 12. (b) Farina, V.; Krishnan, B.; Marshall, D.R.; Roth, G.P. *J. Org. Chem.* **1993**, *58*, 5434.

81. Seitz, D. E.; Lee, S-H.; Hanson, R. N.; Bottaro, J. C. *Syn. Comm.*, **1983**, *13*, 121.

82. Yang, J.S.; Swager, T.M. *J. Am. Chem. Soc.* **1998**, *120*, 11864.

83. (a) Bumm, L.A.; Arnold, J.J.; Cygan, M.T.; Dunbar, T.D.; Burgin, T.P.; Jones, L.; Allara, D.L.; Tour, J.M.; Weiss, P.S. *Science* **1996**, *271*, 1705. (b) Samori, P; Francke, V.; Müllen, K.; Rabe, J.P. *Chem. Eur. J.* **1999**, *5*, 2312. (c) Samori, P.; Sikharulidze, I.; Francke, V.; Müllen, K.; Rabe, J.P. *Nanotechnology* **1999**, *10*, 77. (d) Samori, P; Francke, V.; Müllen, K.; Rabe, J.P. *Thin Solid Films.* **1998**, *336*, 13. (e) Samori, P; Francke, V.; Mangel, T.; Müllen, K.; Rabe, J.P. *Opt. Mater.*. **1998**, *9*, 390. (f) Müllen, K.; Rabe, J.P. *Ann. N.Y. Acad. Sci.* **1998**, *852*, 205.

84. Lakmikantham, M.V.; Vartikar, J.; Kwan, Y.J.; Cava, M.P.; Huang, W.S.; MacDiarmid, A. *Polym. Prepr. (Am. Chem. Soc., Div. Poly. Chem.)* **1983**, *24*, 75.

85. Hsieh, B.R. *Poly. Bull.*, **1991**, *25*, 177.

86. (a) Tateishi, M.; Nishihara, H.; Aramaki, K. *Chem. Lett.*, **1987**, 1727. (b) Kahata, T.; Oosawa, T. JP-Patent 63 205,052 [88 205,052]; *Chem. Abstr.,* **1989**, *110*, 26700.

87. Schopov, I.; Vodenicharova, M. *Makromol. Chem.*, **1978**, *179*, 63.

88. Agrawal, A.K.; Jenekhe, S.A. *Chem. Mater.,* **1992**, *4*, 95.

89. (a) Dieck, H.A.; Heck, R.F. *J. Organomet. Chem.* **1975**, *93*, 259. (b) Cassar, I. *J. Organomet. Chem.* **1975**, *93*, 253. (c) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467.

90. Osakada, K.; Sakata, R.; Yamamoto, T. *Organometallics* **1997**, *16*, 5354.

91. Giesa, R.; Schulz, R.C. *Macromol. Chem. Phys.* **1993**, *191*, 857.

92. Moroni, M.; LeMoigne, J.; Luzzati, S. *Macromolecules* **1994**, *27*, 562.

93. (a) Ofer, D.; Swager, T.M.; Wrighton, M.S. *Chem. Mater.* **1995**, *7*, 418. (b) Swager, T.M.; Gil, C.J.; Wrighton, M.S. *J. Phys. Chem.* **1995**, *99*, 4886.

94. (a) Weder, C.; Wrighton, M.S. *Macromolecules* **1996**, *29*, 5157. (b) Weder, C.; Wrighton, M.S.; Spreiter, R.; Bosshard, C.; Günter, P. *J. Phys. Chem.* **1996**, *100*, 18931.

95. Steiger, D.; Smith, P.; Weder, C. *Macromol. Rapid Commun.* **1997**, *18*, 643.

96. Kim, J.S.; McHugh, S.K.; Swager, T.M. *Macromolecules* **1999**, *32*, 1500.

97. Li, H.; Powell, D.R.; Hayashi, R.K.; West, R. *Macromolecules* **1998**, *31*, 52.

98. Yang, J.S.; Swager, T.M. *J. Am. Chem. Soc.* **1998**, *120*, 5321.

99. Zhou, Q.; Swager, T.M. *J. Am. Chem. Soc.* **1995**, *117*, 12593.

100. Francke, V.; Mangel, T.; Müllen, K. *Macromolecules* **1998**, *31*, 2447.

101. a) Giesa, R. *J.M.S.-Rev. Macromol. Chem. Phys.* **1996**, *36*, 631. (a) Bunz, U.H.F. *Chem. Rev.* **2000**, *100*, 1605.

102. (a) Ley, K.D.; Whittle, C.E.; Bartberger, M.D.; Schanze, K.S. *J. Amer. Chem. Soc.* **1997**, *119*, 3423. (b) Walters, K.A.; Ley, K.D.; Schanze, K.S. *J. Chem. Soc., Chem. Commun.* **1998**, *10*, 1115. (c) Ley, K.D.; Schanze, K.S. *Coordination Chem. Rev.* **1998**, *171*, 287. (d) Ley, K.D.; Walters, K.A.; Schanze, K.S. *Synthetic Metals.* **1999**, *102*, 1585. (e) Ley, K.D.; Li, Y.T.; Johnson, J.V.; Powell, D.H.; Schanze, K.S. *J. Chem. Soc., Chem. Commun.* **1999**, *17*, 1749.

103. Johnstone, R.A.W.; Rose, M.E. *Tetrahedron* **1979**, *35*, 2169.

104. (a) Rau, I.U.; Rehahn, M. *Acta Polymer.* **1994**, *45*, 3. (b) Brodowski, G.; Horvath, A.; Ballauff, M.; Rehahn, M. *Macromolecules* **1996**, *29*, 6962.

105. Huenig, S.; Bau, R.; Kemmer, M.; Meixner, H.; Metzenthin, T. *Eur.J.Org.Chem.* **1998**, *2*, 335.

106. Saraf, T. *Pak. J. Sci. Ind.Res.* **1972**, *15*, 160.

BIOGRAPHICAL SKETCH

Michael Brian Ramey, son of James Bobby and Jewell Sue Ramey, was born on July 24, 1973 in Kingsport, TN. Michael attended Powell Valley High School in rural Big Stone Gap, Virginia, where he graduated valedictorian of a class of 169 students. After attending a small liberal arts college for two years, Michael transferred to Virginia Polytechnic and State University (VA Tech) in 1993. At VA Tech, Michael was an active member of Alpha Chi Sigma, a professional co-educational chemistry fraternity and performed basic undergraduate work for Dr. Judy Riffle. Michael graduated *summa cum laude* with a Bachelor of Science degree in chemistry in 1996. After spending the summer performing research for Milliken and Company in Spartanburg, South Carolina, Michael arrived in Gainesville during August 1996 to begin his endeavor to become a professional chemist. During the course of graduate school, Michael joined the research group of Dr. John Reynolds, married Jennifer Carol Shelton in 1997, and is awaiting the arrival of his first child in September 2001. Michael is a participant in the Palace Knight Program with the United States Air Force, which has provided institutional and salary funding through the final two years of graduate school. Post graduation in May 2001, the Ramey family will reside in Dayton, Ohio, as Michael becomes a member of the research laboratories at Wright Patterson Air Force Base.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

John R. Reynolds, Chair
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Kenneth B. Wagener
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Kirk S. Schanze
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Daniel R. Talham
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Anthony B. Brennan
Associate Professor of Materials
Science and Engineering

LD
1780
20 .01
.R172

UNIVERSITY OF FLORIDA
3 1262 08554 4509